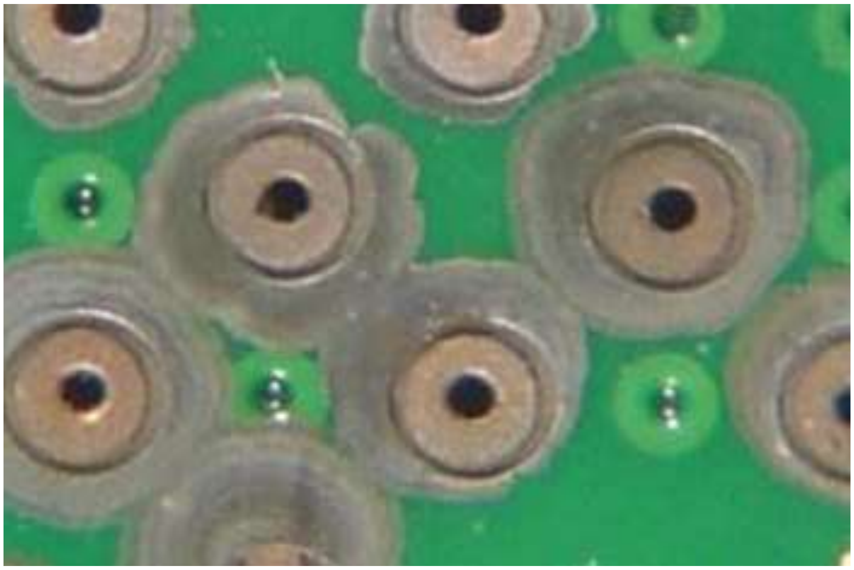
PROJECT REPORT

Qualification Test Development for Creep Corrosion

AUGUST 2018



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EXECUTIVE SUMMARY

Creep corrosion is not a new phenomenon, it has become more prevalent since the enactment of the European Union's Restriction of Hazardous Substance (RoHS) Directive on 1 July 2006. The directive bans the use of lead and other hazardous substances in products (where lead-based surface finishes offered excellent corrosion resistance). The higher melting temperatures of the lead-free solders and their poor wetting of copper metallization on PCBs forced changes to PCB laminates, surface finishes and processing temperature-time profiles. As a result, printed circuit boards might have higher risk of creep corrosion.

Information technology equipment must be qualified to operate reliably in data and telecom centers located worldwide, especially in the expanding markets, such as Asia, where environments are often humid and/or have high levels of sulfur-bearing pollution. The main pollutants causing corrosion are sulfur-bearing gases and oxidizing gases such as ozone and nitrogen oxides. One of the common modes of corrosion-related failures is creep corrosion which is the corrosion of copper and silver metallization on printed circuit boards (PCBs) and the surface migration of their mostly sulfide corrosion products to such an extent that they bridge and electrically short circuit neighboring features on the boards.

The International Electronics Manufacturing Initiative (iNEMI) organized a project — the Qualification Test Development for Creep Corrosion — to improve industry understanding of the factors affecting creep corrosion on PCBs and printed circuit board assemblies (PCBAs). The project also focused on developing a qualification test to determine whether products will suffer creep corrosion in the field, especially in geographies heavily polluted with sulfur-bearing gaseous contamination. A major byproduct of the multiphase iNEMI project was the development of an innovative flowers-of-sulfur (FoS) corrosion chamber in which temperature, sulfur content and relative humidity could be well-controlled, and creep corrosion with morphology similar to that in the field could be reproduced. The starting point for the chamber design was the ASTM B809 - 95(2013) Standard Test Method for Porosity in Metallic Coatings by Humid Sulfur Vapor ("Flowers-of-Sulfur") which describes a desiccator vessel containing sulfur and saturated KNO_3 saturated salt solution for testing the porosity in gold plating over copper substrates. The chamber developed by the iNEMI team uses flowers of sulfur as the source of sulfur gas, a saturated salt solution to maintain constant humidity and a household bleach as the source of chlorine gas. The resulting chamber is inexpensive to build and easy to maintain and can serve as a useful, general-purpose corrosion chamber for testing electronic hardware.

The effort of developing the iNEMI FoS chamber-based creep corrosion test led to several discoveries:

- Chlorine concentration in the chamber decreases dramatically with increasing relative humidity.
- The corrosivity of the chamber air decreases dramatically with PCB loading.
- Prebaking the test circuit boards under flowing nitrogen gas at 100°C for 24 hours is a necessary condition in this test for creep corrosion occurrence — it may have significantly reduced the VOCs coming off the PCBs.
- Creep corrosion can occur on some PCB finishes at very low relative humidity levels and on others at high humidity levels.
- Creep corrosion emanates primarily from where the solder mask overlaps the copper metallization.
- A two-year storage period may reduce the propensity to creep corrosion. This discovery was based on two production circuit boards that had suffered creep corrosion in the field and in the iNEMI

FoS chamber when the PCBs were new. After being stored for two years in an office environment, the circuit boards stopped suffering creep corrosion in the iNEMI FoS chamber.

Based on these discoveries, the iNEMI creep corrosion qualification test includes the following:

- Prebake the test PCBs under flowing nitrogen gas at 100°C for 24 hours to eliminate the impact of VOCs.
- Run three five-day tests in an iNEMI FoS chamber, inspecting the PCBs after each test run for creep corrosion.
- Maintain a different level of relative humidity (RH) in each of three test runs, using a different saturated salt solution.
- Pass-fail criterion is the occurrence of creep corrosion bridging the gap between neighboring metallization features on the test PCB.

The qualification test was successfully used in two round-robin tests at three companies on test PCBs from two different lots, with three different finishes (ImAg, ENIG and OSP) and soldered with two different fluxes (rosin flux and organic acid flux). In the first round-robin, the ENIG-finished boards suffered the most creep corrosion and the OSP-finished boards suffered the least. In the second round-robin test, the ImAg-finished boards suffered more creep corrosion than the ENIG-finished boards, and the OSP-finished boards suffered the least. This difference may be a natural outcome of the aging of the PCBs. It was observed that PCBs from lots that had suffered creep corrosion in the field stopped suffering creep corrosion after two years of storage in an office environment. In other words, creep corrosion behavior changes as PCBs age.

The iNEMI FoS chamber has the potential for use as a general-purpose corrosion chamber. It has been used to determine the corrosion rates of copper and silver as a function of temperature and humidity. This is the first thorough study of copper and silver corrosion rates.

The importance of the iNEMI corrosion chamber in ensuring high reliability of electronic products cannot be over emphasized considering that to remain on the Moore's Law performance curve attention has shifted to packaging miniaturization through dramatic changes in packaging technologies. It behooves the industry to reduce the reliability risks of these new technologies by qualifying them against corrosion-related failures, especially in geographies with high levels of pollution and relative humidity.

1. Project scope

Creep corrosion on PCBs is the corrosion of the PCB metallization and the spreading of the corrosion products, mostly copper and silver sulfides, across the PCB surfaces to the extent that the spreading corrosion products electrically short-circuit the neighboring metallic features on the PCB. iNEMI began its study of this phenomenon in 2009. The initial experimental program used a mixed flowing gases (MFG) test chamber to study creep corrosion. Then in 2013, iNEMI launched the Qualification Test Development for Creep Corrosion Project which explored the use of flowers of sulfur (FoS) test chamber for creep corrosion. The objective of this iNEMI project was to improve industry understanding of the factors affecting creep corrosion on printed circuit boards (PCBs) and printed circuit board assemblies (PCBAs) and to develop a test to qualify products that would not suffer creep corrosion in the field even in geographies heavily polluted with sulfur-bearing gaseous contamination.

Project deliverables included the following:

1. Understanding the effects of PCB surface finishes, soldering fluxes, relative humidity and storage time on creep corrosion in environments containing high concentrations of sulfur-bearing gaseous contamination.
2. A low-cost, easy-to-execute, industry-standard creep corrosion qualification test.

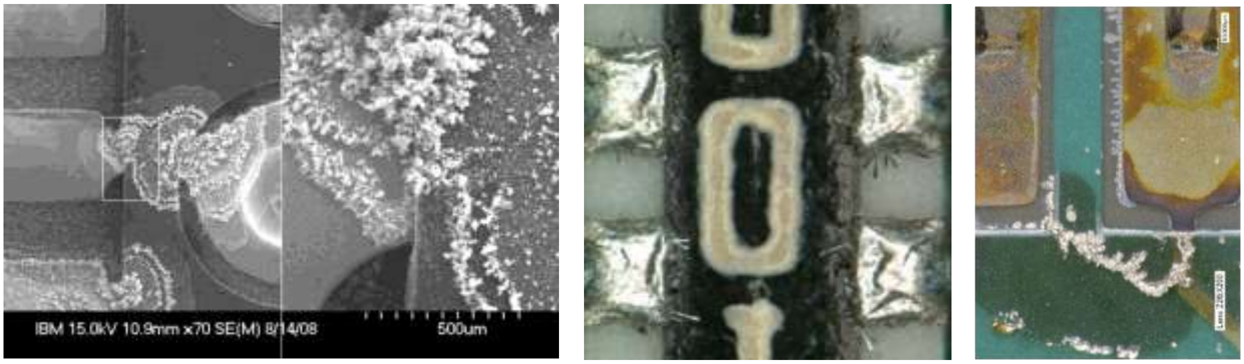
Test development was completed over three phases of the project:

- Phase 1: Test chamber design and preliminary test (2013-2014)
- Phase 2: Six test runs to study test setup effectiveness (2014-2015)
- Phase 3: Determine the effect of relative humidity on creep corrosion, finalize the creep corrosion qualification test and round-robin test for reproducibility in different laboratories (2016-2017).

The project strategy was as follows:

- Develop a low-cost, convenient-to-use, general-purpose corrosion chamber in which
    a. the sulfur and chlorine concentrations and relative humidity can be reasonably controlled at a constant 50°C chamber temperature;
    b. the relative humidity can be controlled at various incremental values in the 11-90% range;
    c. the gaseous concentration and humidity can be reasonably uniformly distributed in the chamber; and
    d. there can be controlled air flow over the test specimens in the chamber.

2. Develop a means by which the volatile organic compounds (VOCs) coming off the test specimens do not contaminate the corrosion chamber.
3. Study the effects of PCB surface finishes, soldering fluxes, PCB design features, relative humidity and store time on creep corrosion.
4. Develop a creep corrosion qualification test.
5. Evaluate the creep corrosion qualification test using round-robin testing.



(a) Creep corrosion (b) Corrosion of silver termination in resistors (c) Silver migration

Figure 2.1: Common modes of corrosion-related failures of IT equipment in data centers [12]

By expanding industry's understanding of the effects of various factors on creep corrosion, the project team aimed to help companies avoid creep corrosion on PCBs in environments with high levels of sulfur-bearing gaseous contamination.

2. Background

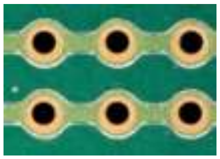
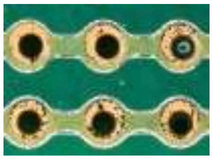
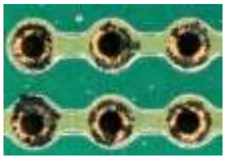
2.1 Corrosion-related failures

IT equipment may encounter corrosion-related failures in data and telecom centers with high levels of atmospheric pollution and high relative humidity levels as are commonly found in expanding markets, in regions such as Asia. The main pollutants are sulfur-bearing gases and oxidizing gases such as ozone and nitrogen oxides. The common failures modes, shown in **Figure 2.1**, are: (a) electrical short circuits due to creep corrosion on PCBs; (b) electrical open circuits due to corrosion of silver terminations in surface-mount resistors; and (3) electrical short circuits due to silver migration on PCBs.

Pass/fail criterion

Any observation of creep corrosion that substantially bridges the gap between features on a PCB would be a cause for rejection of the PCB. The acceptable extent of creep corrosion must be defined and accepted by the PCB manufacturer and procurer. As an example, an acceptable extent of creep corrosion may be one that bridges less than one-third of the gap between the PCB features. The visual inspection criteria and rankings are shown in **Table 2.1**.

Table 2.1: Visual inspection criteria and rankings

Rank 0	Rank 1	Rank 2	Rank 3	Rank 4
No Corrosion	Local Corrosion	Light Creep Corrosion (<1/3 gap)	Moderate Creep Corrosion (>1/3 gap)	Heavy Creep Corrosion
				
Oxidation or tarnishing is OK.	Corrosion limited to pads or holes only, no spread.	Corrosion spreading from pads or holes, but not bridging between features.	Corrosion spreading from pads or holes, but not bridging between features.	Severe corrosion, bridging between features.
Pass	Pass	Pass	Fail	Fail

History of creep corrosion

The history of creep corrosion, the acceptable levels of corrosivity of data center air and the various ways of testing for creep corrosion are described in this section. Tin-lead (SnPb) was the solder alloy of choice for PCB assemblies since the dawn of the electronic age. Tin-lead solder wets copper metallization on PCBs well and is resistant to corrosion even in very harsh environments. The European Union's Restriction of Hazardous Substance (RoHS) Directive, which took effect on 1 July 2006 **[1]**, severely restricted the use of Pb in solder and the use of SnPb as PCB surface finish. The Pb-free solders that replaced SnPb typically contain tin (Sn), silver (Ag) and copper Cu) and are known as "SAC" solders.

Furthermore, high density circuit and fine pitch devices requires coplanar PCB finishes, which resulted in the development of several alternate PCB finishes. These included electroless nickel immersion gold (ENIG), immersion silver (ImAg), immersion tin (ImSn) and organic solderability preservative (OSP) **[2]**. While effort was focused on assembly issues, the corrosion concern was somewhat neglected. The move to SAC soldered PCBs was not considered different enough to warrant an industry-wide, thorough corrosion study.

A taskforce, which later became the IPC 3-11g Metal Finishes Data Acquisition Group, worked with Underwriters Laboratories (UL) and proposed an exemption to the UL-796 test for electrochemical migration. Extensive testing had demonstrated that electrochemical migration was not an issue with ImAg finish on PCBs **[3]**. Unfortunately, concern was not raised that creep corrosion may occur on the PCBs with new finishes coming online, even though creep corrosion was a known phenomenon. It was known to occur on integrated circuit (IC) plastic packages and on gold- and palladium-plated electrical contacts **[4]**. Failure could occur if the sulfide corrosion product bridged and thus electrically shorted the neighboring features on a PCB. The first reported evidence of creep corrosion on PCB surfaces was probably by Veale in 2005 **[2]**. Creep corrosion failure of Pb-free boards with ImAg finish was reported in industrial environments high in sulfur-bearing gaseous pollution. Following the creep corrosion experience in the field, Veale subjected test boards with various finishes to a mixed flowing gas (MFG) environment **[5]** and reported that no Pb-free board would survive Instrument Society of Automation (ISA) 71.04-1985 severity level G3 **[6]**, and that ENIG and ImAg boards would not even survive ISA severity level G2. ISA severity levels are described later in this section. Interestingly, during the same year (2005), Cullen reported that typical MFG environment testing did not produce creep corrosion on Pb-free PCBs **[7]**. The first reported creep corrosion on PCBs in computer hardware was probably by Mazurkiewicz **[8]** who in 2006 reported that the move to ImAg and OSP board finishes, motivated by compliance with RoHS, dramatically increased the computer early life failures due to copper creep corrosion emanating from exposed copper on PCBs, especially inside the plated-through barrels. The challenge of testing for creep corrosion was highlighted in a 2007 paper by Schueller **[9]** that Pb-free desktops that had been thoroughly qualified with a regimen of tests started failing in the field within two to four months of being put in service. The awareness that creep corrosion on Pb-free PCBs is highly surface sensitive was reported by Xu et. al. in 2007 and 2009 **[10, 11]**. The work reported the following general observations: PCBs with clean FR4 and clean solder mask surfaces were found not to suffer creep corrosion; organic acid wave soldering flux residues supported creep corrosion; rosin-based wave soldering fluxes and rosin-based solder paste are resistant to creep corrosion; and MFG testing provides a realistic accelerated test for creep corrosion. Later works by Yin et al and Singh et al demonstrated that chloride contamination or ammonium sulfate (major component in environmental dust) contamination also make a PCB surface creepable and promote creep corrosion **[19, 39, 45]**.

Table 2.2: Gaseous corrosivity levels ISA 71.04 standard [12]

Severity level	Reactivity level	ISA 71.04-1985	ISA 71.04-2013	
		Copper corrosion rate, Å/month	Copper corrosion rate, Å/month	Silver corrosion rate, Å/month
G1	mild	<300	<300	<200
G2	moderate	300-1000	300-1000	200-1000
G3	harsh	1000-2000	1000-2000	1000-2000
GX	severe	>2000	>2000	>2000

The restriction on the use of lead in solders in electronics occurred as the electronic market in Asia was expanding at a rapid rate. The combination of the poor creep corrosion resistance of the Pb-free PCB assemblies and the proliferation of electronics in the Asian geographies, high in humidity as well as sulfur-bearing gaseous pollution, led to a dramatic rise in the PCB failure rates due to creep corrosion. Suddenly, there was a need for a corrosion test to ensure their survival in harsh sulfur-bearing environments. There was also a need to define a gaseous contamination limit in which electronics could operate reliably. Various technical committees, including those of ASHRAE, IPC, ISA and iNEMI, became active in this arena.

In 1985, the International Society for Automation (ISA) came up with standard 71.04-1985 that classified the corrosivity of air into four categories, listed in **Table 2.2**. The classification was based on the corrosion rates of copper in Å/month. As shown in the table, severity level G1, corresponding to copper corrosion rates of less than 300 Å/month, was considered acceptable for electronic equipment. In 2009, ASHRAE (American Society of Heating, Refrigerating and Air-Conditioning Engineers) conducted a worldwide survey of the corrosion rates of copper and silver in data centers with and without creep corrosion failures and concluded that for the environment to be acceptable for modern electronics, the rate of silver corrosion should be less than 200 Å/month and that of copper should be less than 300 Å/month. ASHRAE published the survey results in a white paper in 2009 and revised it in 2011 **[13]**, and iNEMI released position statement in 2012 (see Appendix B) on the Limits of Temperature, Humidity and Gaseous Contamination in Data Centers and Telecomm Office to Avoid Creep Corrosion on Printed Circuit Boards which supports ASHRAE white paper findings and recommendations. In response, the ISA standard was modified in 2013. The new ISA standard 71.04-2013 includes the change to the G1 severity level as shown in **Table 2.2**, which states that for the data center environment to be acceptable for modern electronics the copper and silver corrosion rates should be less than 300 Å/month and 200 Å/month, respectively.

The challenge remained to develop a test that suppliers of Pb-free PCB assemblies could use to satisfy customers that their products would survive moderately corrosive environments as defined in the 2011 ASHRAE white paper and in the ISA 71.04-2013 standard as having silver and copper corrosion rates less than 1000 Å/month. There are three well-known environmental chambers that can be used for creep corrosion studies: (1) mixed flowing gas (MFG), (2) Chavant-clay, and (3) flowers-of-sulfur (FoS).

2.2 Existing test methods

Mixed flowing gas test

The MFG test is a laboratory accelerated test intended to simulate contaminated industrial environments. The device under test is placed in a chamber with controlled temperature, relative humidity and predetermined concentrations (at ppb levels) of the following gaseous pollutants: H_2S, Cl_2, NO_2 and SO_2. MFG test standards were developed in the 1980s by various organizations, including Battelle Labs (Columbus, OH) **[5]**, American Society for Testing and Material (ASTM) **[14]**, Electronic Industries Association (EIA) **[15]**, International Electrotechnical Commission (IEC) **[16]**, Telcordia (previously Bellcore) **[17]** and IBM **[18]**.

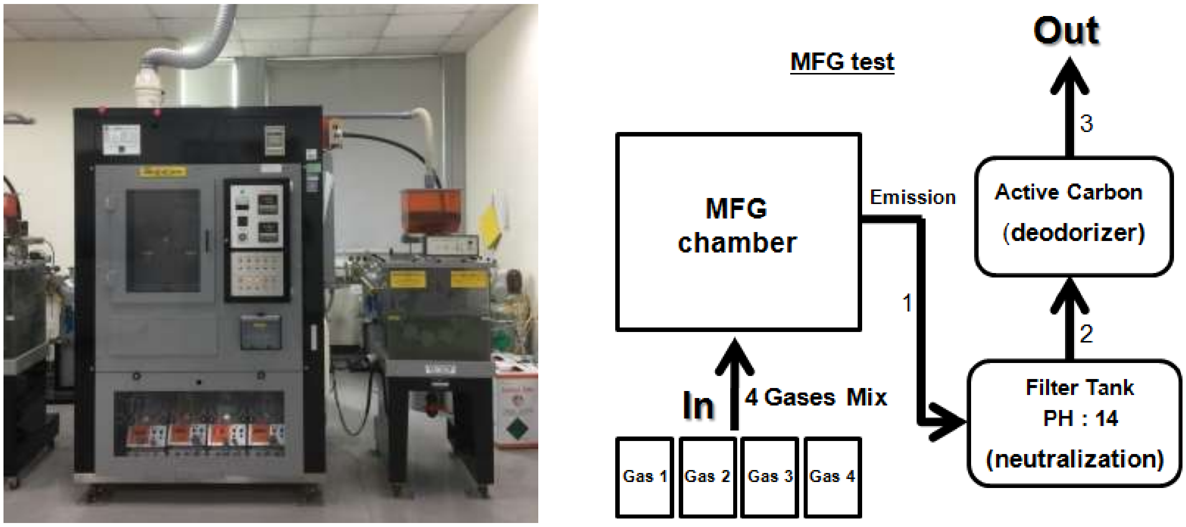


Figure 2.2: Typical mixed flowing gas (MFG) chamber and flowchart

In general, the MFG test has better control over the gas concentrations than the FoS and Chavant clay tests. The three-phased iNEMI project, which was started in 2009, initially studied creep corrosion on PCBs using MFG **[19-22]**. The project team completed its objectives with an end-of-project webinar in November 2012 with summary and conclusions as follows:

1. MFG test conditions were chosen to reach the target copper corrosion rate of 5000 Å/month.
2. The five PCB finishes tested were ImAg, OSP, Pb-free HASL, ImSn and ENIG. The PCBs soldered using organic acid flux suffered the most creep corrosion. Pb-free HASL-finished PCBs soldered with rosin flux suffered very little creep corrosion. ImSn-finished PCBs suffered the least creep corrosion.
3. Organic acid-fluxed PCBs suffered more creep corrosion than rosin-fluxed PCBs.
4. Both rosin fluxes with lower and higher rosin content showed similar creep corrosion results.

iNEMI project results **[19-22]** and the pioneering works by Veale **[2]** and Xu **[10-11]** showed that MFG is a viable test for creep corrosion qualification. The downside of the MFG test is the limited availability of MFG chambers and their high maintenance and run costs. **Figure 2.2** shows a typical setup for a mixed flowing gas chamber.

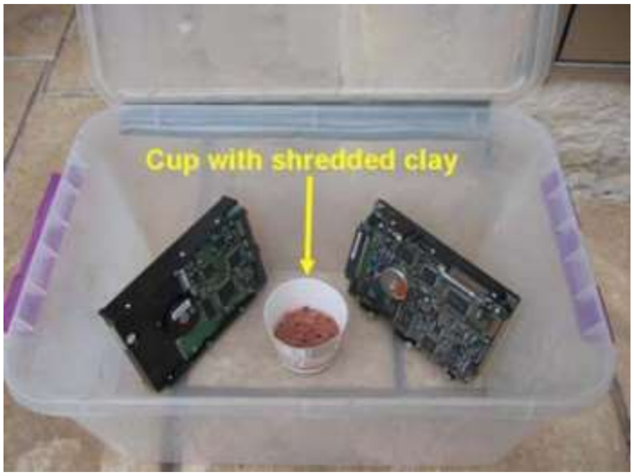


Figure 2.3: Typical Chavant-clay chamber

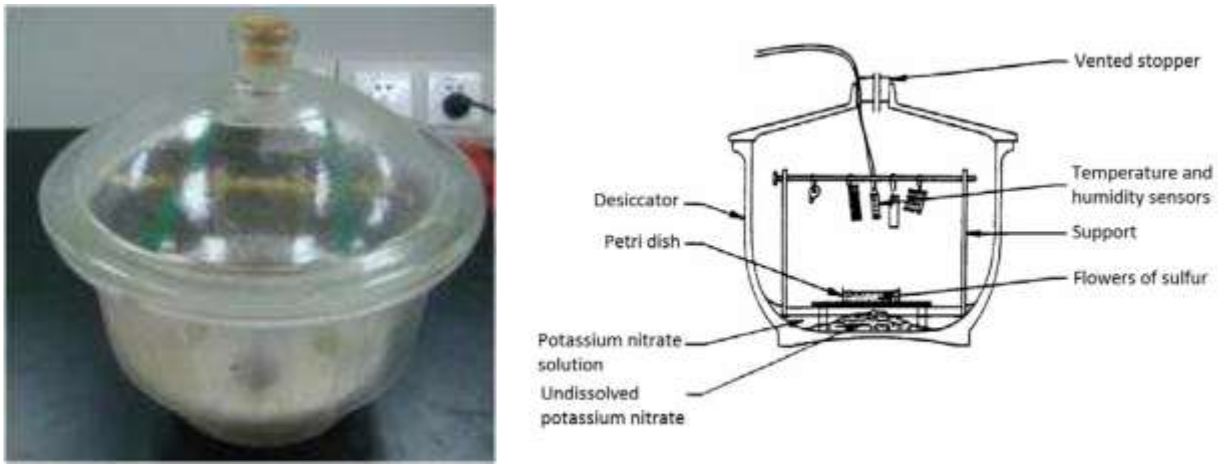


Figure 2.4: Typical ASTM flowers-of-sulfur (FoS) chamber [23]

Chavant-clay test

Another test method that was explored in early creep corrosion studies was the clay test described by Schueller in 2007 **[9]**. Chavant clay (type J-525), a sulfur-bearing clay, was used as the source of sulfur gas. The wetted clay releases sulfur gas when heated to 45-55ºC. The test PCBs and the wetted clay are sealed in a plastic container, as shown in **Figure 2.3**, and heated in a microwave oven until the clay reaches 50ºC. The clay is reheated every 12 hours to release more sulfur gas. Creep corrosion was observed on ImAg-finished PCBs after two days and the extent of creep corrosion became quite pronounced after five days. The OSP-finished PCBs suffered slight creep corrosion in six days, while the lead-free hot air surface level (HASL)-finished PCBs suffered no creep corrosion. Since this work, there is no known additional published work on optimizing the technique partly because the test conditions, such as the relative humidity and the sulfur content, cannot be readily controlled.

Flowers-of-sulfur test

The iNEMI flowers-of-sulfur (FoS) test method, which is the subject of this white paper, overcomes many of the shortcomings of the MFG and the Chavant-clay tests. The iNEMI FoS test is relatively inexpensive and the test conditions are quite easy to control. The iNEMI FoS test is based on the ASTM B 809-95 standard which originally intended for detection of porosity in metal coatings **[23]**. The ASTM flowers-of-sulfur chamber, shown in **Figure 2.4**, consists of a desiccator at 50ºC containing a dish half full of flowers of sulfur and a saturated solution containing 200 g KNO_3 in the bottom of the vessel. The chamber has sulfur as the only corrosive gas. It does not have any means to stir the air in the chamber or to conveniently support the test specimens. The iNEMI FoS chamber, shown in **Figure 2.5**, a 300mm cube acrylic sealed box, is different in many ways and has many advantages over the ASTM chamber. The iNEMI chamber (a) has 100 ml of Clorox® bleach containing 8.25% sodium hypochlorite as a source of chlorine gas necessary for the synergistic corrosion effect commonly found in the field; (b) provides a paddle wheel to house eight test specimens that also stirs the air in the chamber in a somewhat repeatable manner; and (c) has a very convenient means of loading and unloading the test specimens and for the insertion of sulfur, saturated salt and Clorox at the start of every test. The iNEMI FoS chamber took many years to develop. The details of the design and development of the iNEMI FoS test chamber and the round-robin testing to determine its effectiveness for creep corrosion qualification testing are discussed in the following sections. The effects of humidity, aging of the PCBs and the solder-mask interface on creep corrosion are also presented and discussed.

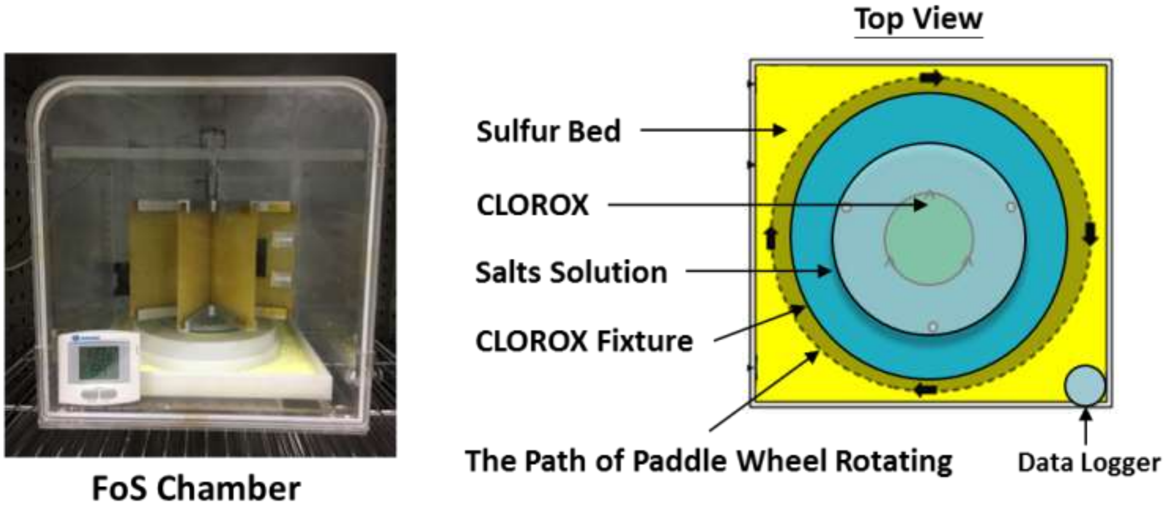


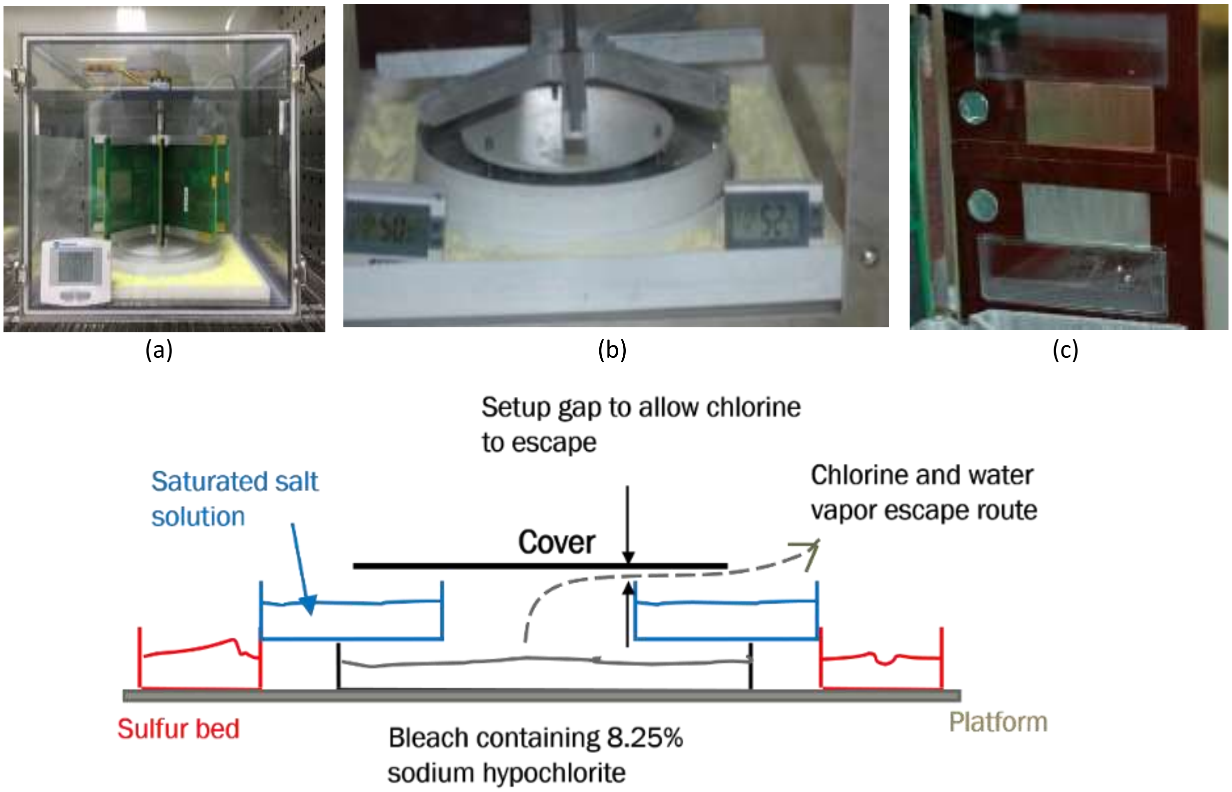
Figure 2.5: iNEMI flowers-of-sulfur (FoS) chamber

3. Qualification test procedure for creep corrosion using FoS chamber

3.1 iNEMI FoS chamber design

The iNEMI FoS chamber, shown in **Figure 3.1a**, is a 300mm cube acrylic box with a paddle wheel rotating at 20 revolutions per minute (RPM) **[24, 25]**. The paddle wheel has eight pairs of slots, and each pair — one on top and one directly below —can accommodate a circuit board. One of the eight pairs of slots is generally reserved for a board on which Cu and Ag foils are mounted for Cu and Ag corrosion rate measurements. This mounting board for the copper and silver foils must be of a material that does not excessively absorb the gases and moisture in the chamber. Copper and silver foils on a mounting board are shown in **Figure 3.1c**. A detailed description of the foils is provided in Section 4 (Corrosion rate measurement).

The Cu and Ag corrosion rates are an indication of the sulfur and chlorine gas concentration in the chamber. One or two temperature and relative humidity probes should be included in the chamber as shown in **Figures 3.1a and 3.1b**. The relative humidity probes must be checked for accuracy by placing them in a sealed desiccator that also contains a saturated salt solution. The relative humidity probe reading should be the deliquescence relative humidity of the saturated salt solution. The setup to control the sulfur and chlorine gas concentrations and the relative humidity in the chamber is described in **Figure 3.1b**. Two hundred grams of sulfur is provided in a 275mm square tray, 20mm deep, with a 195mm circular opening in the center. The sulfur concentration is controlled by placing the chamber in an oven maintained at a constant 50°C. The chlorine gas is provided by 100ml of Clorox®, consisting of an aqueous solution of 8.25% sodium hypochlorite with some NaOH added to control pH. A limited number of bleach formulations were evaluated and "Concentrated" Clorox was identified and used for the experiments reported here (see **Figure 3.2** for a photo of the type of Clorox used and the content label). Other bleach formulations would require further testing. The Clorox is contained in a 145mm diameter petri dish that sits inside the sulfur tray on the same platform as the sulfur tray. The saturated salt solution is in a 190mm diameter tray which sits atop the petri dish containing the Clorox and has a circular, 65mm-diameter opening in the center. The circular opening of the saturated salt solution tray is covered by a circular plate with 1 or 3mm gap to allow controlled escape of the chlorine gas from the Clorox bleach. The Clorox setup is shown in cross section in Figure **3.1d**. The cover plate also throttles the escape of water vapor from the bleach such that the



(a) (b) (c)

(d)

Figure 3.1: (a) iNEMI FoS test chamber loaded with test PCBs. (b) The tray-like Clorox setup below the test PCBs provides the sulfur and chlorine gases and maintains the relative humidity in the chamber at the deliquescence relative humidity of the saturated salt solution in the setup. (c) Copper and silver foils on a board. (d) Schematic of the Clorox setup. [24, 25]

saturated salt solution can dominate the relative humidity in the chamber at its deliquescence relative humidity. The salt solution must always be kept saturated by having enough undissolved salt in the solution. The relative humidity can be maintained at various incremental values in the 11-90% range, depending on the salt solution chosen. The chamber reaches steady state in a few hours. It is most challenging to achieve low humidity in the chamber because of the water vapor given off by the Clorox bleach. The chamber design described here has been able to overcome this challenge. With a zinc chloride saturated solution in the chamber at 50°C, the chamber design allows the humidity to stabilize at 11%, which is the deliquescence relative humidity of $ZnCl_2$.

Figure 3.2: Clorox bottle and chemical label on bottle

3.2 Test procedure

Following is an overview of the qualification test procedure, which uses the iNEMI FOS chamber described previously. For a detailed step-by-step description of the process, see Appendix A.

1. Prebake test PCBs at 100°C in flowing nitrogen gas for 24 hours to eliminate the impact of volatile organic compounds (VOCs).
2. Load paddle wheel with seven test PCBs plus one board on which Cu and Ag foils are mounted for Cu and Ag corrosion rate measurements. (Mounting board must be of a material that does not excessively absorb the gases and moisture in the chamber.)
3. Expose PCBs to three five-day runs at 50°C, each at different levels of relative humidity:
    - Run 1: 31% RH using $MgCl_2$ saturated salt solution
    - Run 2: 59% RH using $NaNO_2$ saturated salt solution
    - Run 3: 81% RH using KCl saturated salt solution
4. Copper and silver corrosion rates and rate of formation of AgCl measured using coulometric reduction and mass gain methods. Photograph and record the corrosion failures.

4. Corrosion rate measurement

The corrosion rates of copper and silver are a measure of the corrosivity of the FoS chamber environment and of how well the chamber conditions are controlled. Precedence exists for such an approach. As mentioned previously, the 2011 ASHRAE white paper on data center gaseous and particulate guidelines states that for a data center environment to be acceptable, the copper and silver corrosion rates should be less than 300 Å/month and 200 Å/month, respectively **[26]**. Rather than measure the gaseous composition, which is typically in the low ppb range and is a difficult task in the best of conditions, the reactive monitoring approach proposed here relies on the metal corrosion rates as an indirect measure of the environmental conditions. This approach encompasses all factors affecting metal corrosion rates including gaseous composition, temperature, relative humidity and air velocity.

Precleaned silver and copper foils are used to measure mass gain and/or coulometric reduction in order to determine corrosion rate. In both approaches, the metal foils are exposed to the FoS chamber environment under the same airflow conditions as the PCBs under test. The duration of exposure is typically five days, though one day would also be adequate to make relatively accurate measurements. In the mass gain approach, the mass gain of the foils due to corrosion is converted to thickness of the corrosion products assuming a certain chemistry of the corrosion products and the specific gravity of those products. In the coulometric reduction approach, the number of coulombs needed to reduce the corrosion products back to metal is used to calculate the thickness of the corrosion products. An advantage of the coulometric reduction approach is that the chemistry of the corrosion products is known by the electrical potentials at which the corrosion products are reduced. The coulometric reduction approach also provides the thickness of the silver chloride, which is a measure of the chlorine gas concentration in the chamber. A third advantage of coulometric reduction is that it can measure the thickness of corrosion products as low as 10 Å. For these reasons, coulometric reduction is the preferred approach to corrosion rate measurement.

4.1 Metal foils and their precleaning

For the corrosion rate measurements, the project team used 99.95% pure silver and 99.99% pure copper foils that were 25.4 x 50.8mm x 0.13mm thick, supplied by Surepure Chemetals (part numbers 3006 and 3007). The preferred method of cleaning the foils is to first degrease in acetone and isopropyl alcohol, then

Table 4.1: The recommended mechanical and chemical cleaning processes for copper and silver foils

Step	Mechanical Cleaning	Chemical Cleaning
1	**Degrease** In acetone and isopropyl alcohol	**Ultrasonic cleaning for 15 minutes** Immerse coupons in acetone
2	**Oxide removal** Wet grind with 600-grit abrasive paper using deionized (DI) water	**Rinse 60 seconds** In isopropyl alcohol
3	**Rinse for 20 seconds** In deionized water	**Rinse for 60 seconds** In DI water
4	**Rinse for 20 seconds** In acetone and isopropyl alcohol	**Oxide removal for 15 seconds** In 5 vol% HNO_3
5	**Drying** Blow dry using oil-free inert gas	**Rinse 60 seconds** In running overflow DI water
6	**Storage** In desiccators with N_2 gas purge or desiccant	**Rinse for 60 seconds** In isopropyl alcohol
7		**Drying treatment 1 hour** In oven at 60°C with N_2 gas flow

mechanically clean by grinding using de-ionized water wetted 600-grit metallographic grade abrasive paper followed by rinsing in de-ionized water and then in acetone and isopropyl alcohol, and finally blow drying using compressed oil-free inert gas.

The decision on mechanical cleaning using 600-grit metallographic grade abrasive paper as the preferred cleaning method was based on x-ray photoelectron spectroscopy (XPS) studies of non-treated, chemically cleaned and mechanically cleaned silver foils **[27]**. The mechanical and chemical cleaning processes that were studied are described in **Table 4.1**. **Figure 4.1** shows the results of XPS studies of the non-treated and the cleaned silver foils. Both the non-treated and the chemically cleaned silver foils showed presence of surface silver oxide. The oxide could be removed by a 10-second sputter etch. The mechanically cleaned silver foils showed no presence of oxide on the silver foils.

4.2 Mass gain method

Mass gain is a quick and easy method for determining metal corrosion rate as described in ASTM B810-01a **[28]**. The mass gain from exposure to the environment under test can be used to determine the metal corrosion product thickness and hence the corrosion rate. The following calculation is an example of the conversion of silver foil mass gain in μg to the silver sulfide corrosion product (Ag_2S) thickness, T, in angstroms (Å), with the assumption that silver sulfide is the only compound in the corrosion product.


O1s: Chemical Etching (0sec)

O1s: Mechanical Polishing (0sec)

O1s: Non-Treatment (0sec)

No metal oxide was detected!

O1s: Chemical Etching (10sec)

O1s: Non-Treatment (10sec)

Figure 4.1: XPS results for silver foil with various pre-treatments. Chemical etching did not get rid of the surface silver oxide present on non-treated silver. The oxide could be removed by a 10-second sputter etch. Mechanical cleaning removed the surface silver oxide.

$$
\begin{aligned}
T &= \frac{\Delta w}{a}\frac{1}{\rho_{Ag_2S}}\times\left(\frac{m_S+2m_{Ag}}{m_S}\right)\times10^2 \\
&= \frac{\Delta w}{a}\frac{1}{7.23}\times\left(\frac{32.1+2\times107.9}{32.1}\right)\times10^2 \\
&= \frac{\Delta w}{a}\times K_M \\
K_M &= 106.8 \text{ for } Ag_2S \text{ corrosion product}
\end{aligned}
$$

where Δw is the gain of mass, in µg, due to exposure; ρ_{Ag2S} is the specific gravity of Ag_2S; a is the area of the metal foil in cm^2; m_s is the atomic mass of sulfur and m_{Ag} is the atomic mass of silver.

The K_M factor for Cu_2S corrosion product is equal to 88.5. Therefore, if we assume that copper corrodes mostly to Cu_2S, the thickness of the Cu_2S corrosion product in angstroms is equal to ($\Delta w/a$)x88.5.

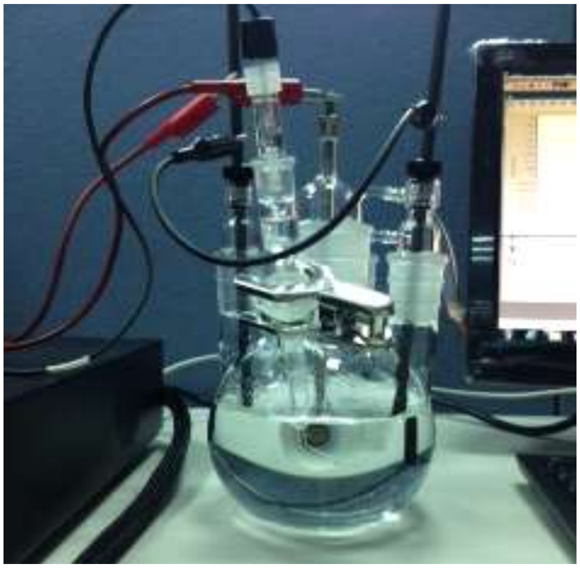
4.3 Coulometric reduction method

Coulometric reduction method is an electrochemical means of identifying and measuring the thickness of the chemical compounds in corrosion products down to tens of angstroms. A low current, typically 50 µA/cm2, is forced through the corrosion product covering the foil immersed in 0.1M KCl electrolyte, while the electrical potential between the foil and the electrolyte is plotted versus time. The galvanostatic curve has a characteristic voltage plateau for each chemical compound being electrochemically reduced to metal. The number of coulombs corresponding to each voltage plateau is a measure of the mass of the chemical compound reduced to metal. For copper, Cu_2O, CuO and Cu_2S can be identified and quantified; for silver, Ag_2S and AgCl can be identified and quantified.

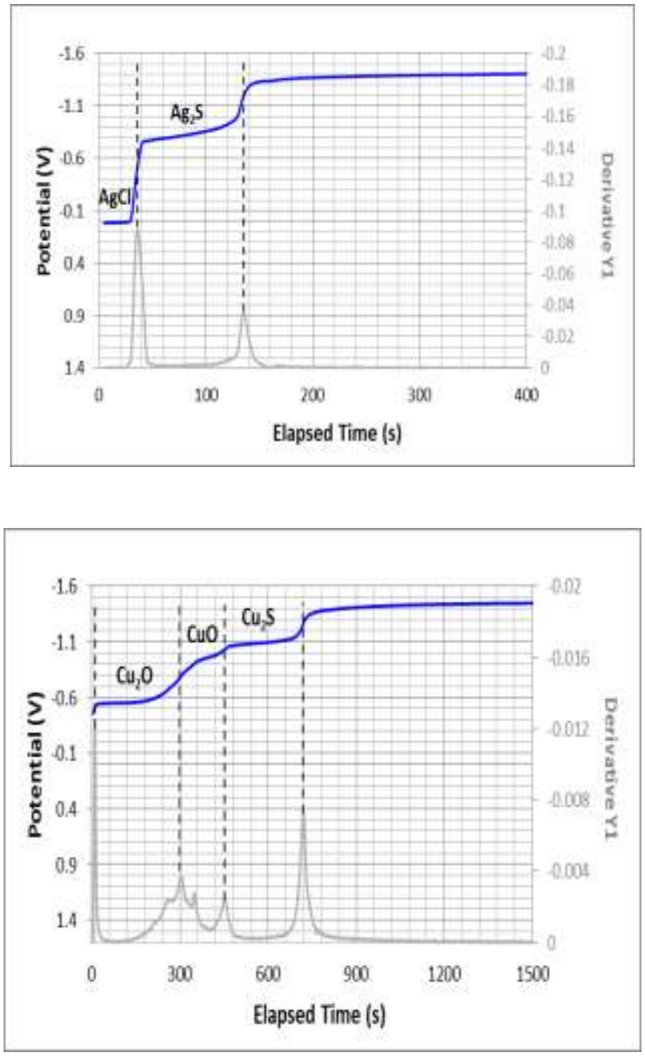
The coulometric reduction procedure is described in detail in ASTM B825-02 **[29]** and in a paper by Krumbien et al **[30]**. For the convenience of the reader, the procedure is described here briefly using the silver corrosion rate measurement as an example. **Figure 4.2a** shows a coulometric reduction setup. The figure also shows a typical coulometric reduction curve for silver and its first derivative. The setup consists of the corroded silver foil, a counter electrode and a calomel electrode, all immersed in KCl electrolyte. The 0.05 mA/cm^2 galvanostatic curve has two voltage plateaus, one for AgCl at about 0 mV and the other at about 800 mV for Ag_2S, both with respect to a saturated Calomel reference electrode. The duration of the plateaus can be determined by taking the first derivative of the galvanostatic curve and measuring the time between the peaks as shown in **Figure 4.2b**. As shown in the figure, the time tAgCl is the silver chloride plateau and the time tAg2S is for the silver sulfide plateau.

The plateau time duration can be converted to corrosion product thickness in angstroms as follows:

$$
\begin{aligned}
\text{Coulombs per cm}^2 &= \frac{i\cdot t}{a\cdot10^3},\ i \text{ is the current in mA and } a \text{ is area in cm}^2 \\
\text{Moles reduced per cm}^2 &= \frac{i\cdot t}{a}\frac{1}{10^3\cdot N\cdot F},\ N \text{ is the valence of the ion being reduced} \\
\text{Mass in grams reduced per cm}^2 &= \frac{i\cdot t}{a}\frac{M}{10^3\cdot N\cdot F},\ M \text{ is corrosion compound molecular masss} \\
\text{Thickness of corrosion product in angstroms} &= \frac{i\cdot t}{a}\frac{M\cdot10^8}{10^3\cdot N\cdot F\cdot d},\ d \text{ is the density of the corrosion compound} \\
&= \frac{i\cdot t}{a}K \\
K \text{ factor for } Ag_2S &= \frac{M\cdot10^8}{10^3\cdot N\cdot F\cdot d} = \frac{(107.9\times2+32.1)\times10^8}{10^3\times2\times96485\times7.23} = 17.8
\end{aligned}
$$



(a) setup



(b) coulometric reduction curves and their derivatives

Figure 4.2: Coulometric reduction setup and coulometric reduction curves for corroded silver and copper foils.

Table 4.2: Densities, molecular mass, reduction potentials and K factor for various corrosion products on Ag and Cu.

Component	Density	Gram-molecular Mass	Reduction Potential* (or Range)	"K" Factor
AgCl	5.56	143.3	0	26.7
Ag_2S	7.23	247.8	0.54-0.82	17.8
Cu_2O	6.0	143.1	0.55-0.75	12.4
CuO	6.4	79.54	0.7-0.9	6.43
Cu_2S	5.6	159.1	1.0-1.15	14.7

- Reduction potentials are dependent on current density and other factors. The values are the approximate midpoint potentials or voltage ranges usually found in a 0.1M KCl electrolyte at a current density of 0.05μA/cm^2 and referred to a Ag/AgCl reference electrode in 0.1M KCl solution.

Reduction potentials and K-factor for several common-corrosive products has been reported by Krumbein et al **[30]**. **Table 4.2** lists factors for calculating mass or thickness of known film components.

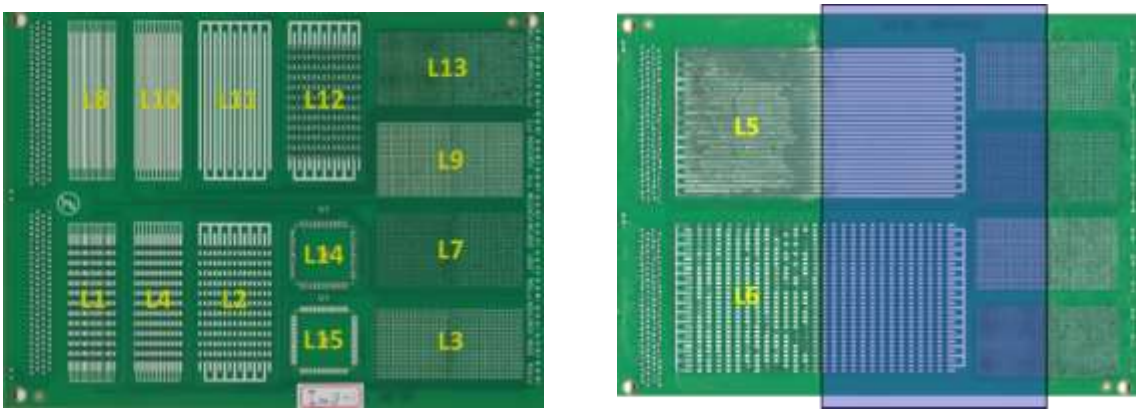
5. Test vehicle design and fabrication

The sections 5 through 9 cover the topics pertinent to the development of a qualification test for creep corrosion on PCBs. These topics include PCB test vehicle design and fabrication (section 5); FoS chamber design and test development (section 6); effect of PCB loading and the role of PCB prebake (section 7); round robin testing of the effect of relative humidity on creep corrosion (section 8); and the round robin testing of the iNEMI FoS creep corrosion qualification test (section 9).

5.1 PCB test vehicle design

The PCB test vehicle used in our project to develop the creep corrosion qualification test was adopted from an Alcatel-Lucent design with some slight modifications **[11, 20]**. The 140mm by 110mm by 1mm thick test PCB features one-half ounce copper on top and bottom and uses a FR4 epoxy compatible with Pb-free soldering. There are 15 land pattern areas on the board with various traces and plated-through via holes (PTHs) with various pitches. This circuit board design makes it convenient for visual inspection and electrical testing for creep corrosion. The areas on the test vehicle shown in **Figure 5.1** are as follows:

- Areas L1, L4 and L2 on top side are comb patterns with solder mask stripes: Area L1 has 0.23mm traces on 0.4mm pitch; area L4 has 0.30mm traces on 0.5mm pitch; and area L2 has 0.66mm traces on 1.27mm pitch.
- Areas L8, L10 and L11 are the same as L1, L4 and L2 but without the solder mask stripes.
- Area L2 is similar to area L12, with the difference that area L2 has no solder paste on it.
- Areas L3, L7, L9 and L13 on top are open via comb pattern on 0.94mm pitch (0.38mm pad-to-pad), 0.81mm pitch (0.25mm pad-to-pad), 0.81mm pitch (0.25mm pad-to-pad) and 0.69mm pitch (0.13mm pad-to-pad), respectively.
- Areas L5 and L6 on the bottom side are comb pattern with 0.66mm traces on 1.27mm pitch. Area L6 has solder mask stripes.
- Areas L14 and L15 have the same land pattern for QFP components. AreaL14 has solder paste deposited on it.


(a) Top Side (Reflow)

(b) Bottom Side (Wave Soldering)

(c) Magnified photo for various PCB pattern

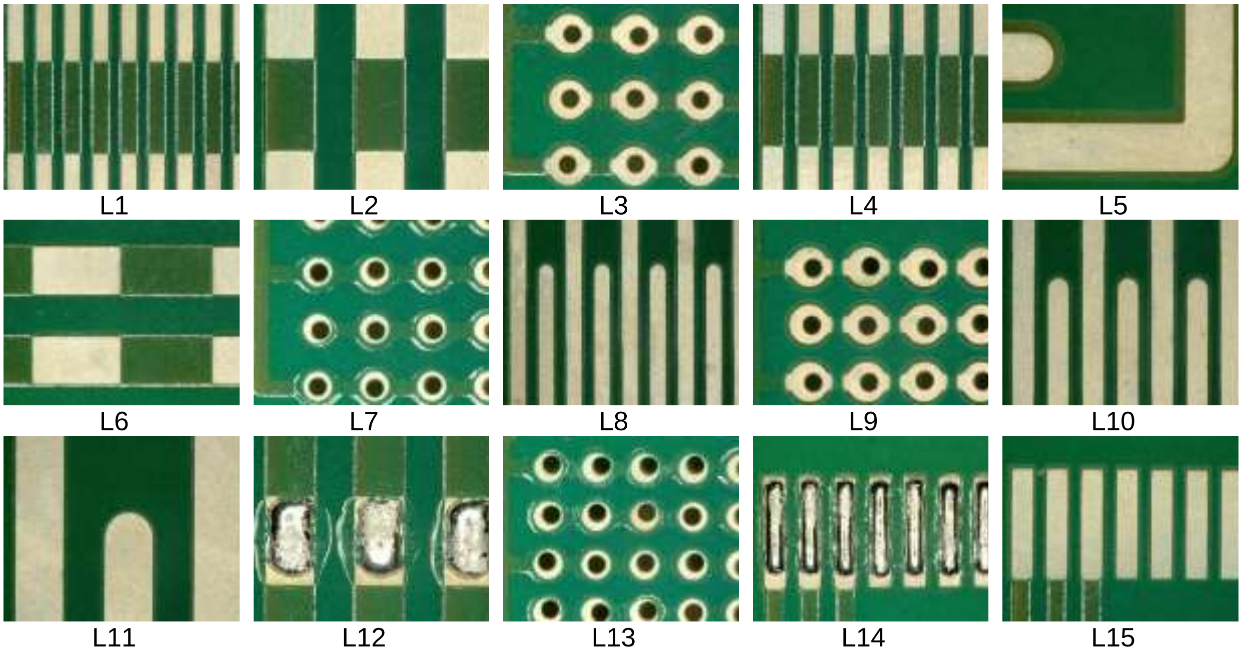


Figure 5.1: Both sides of the test vehicle are shown, with areas numbered. The central area of the bottom side is masked off during the wave soldering process.

5.2 Test board surface finishes

The surface finishes used on the test boards are as follows:

- Immersion silver (ImAg)
- Electroless nickel immersion gold (ENIG)
- Organic solderability preservative (OSP)

5.3 Assembly simulation process: Reflow and wave soldering

A 0.127mm thick stencil is used to print the Pb-free solder paste on the comb pattern at area L12 and on the QFP at area L14 on the top side of the board. These are the only two areas of the test boards with solder paste. A rosin-based, low-activity, halide-free, lead-free (ROL0) SAC305 solder paste is used. The metallization on the other areas of the test boards are not covered with solder paste. A common “tent” type or linear Pb-free reflow profile is used.

After the Pb-free solder paste on the top side of the board is reflowed, the bottom side of the board is wave soldered using a fixture to mask off the center part of the bottom side of the board (as shown in **Figure 5.1**) to simulate the selective wave soldering condition. Because the fixture mask is not in intimate contact with the test boards, some flux invariably gets under the mask and contaminates the board. Two types of no-clean fluxes are used for the wave soldering operation: a low-activity rosin-containing flux, and a VOC-free, halide-free, rosin/resin-free, organic activated flux. Flux is sprayed on the bottom side of the board just prior to the wave soldering. As in real production, some flux flows through the unplugged via to the top side of the board. The SAC305 (96.5% Sn, 3% Ag and 0.5% Cu) alloy is used with the solder pot temperature set at 265°C. The board pre-heat temperature before wave contact is 110°C on the top side of the printed circuit board as specified for the fluxes.

6. FOS chamber design and test development

6.1 Paddle wheel & forced-air setup

The chamber design began with the selection of an acrylic box (Plas Labs, Lansing, Michigan, USA, 800-866-7527) approximately 300mm cube on the inside with 11.5 mm wall thickness and a front gasketed door that could be removed. The door was stiffened by supporting it on its periphery with a stainless-steel picture frame and by adding four spring-loaded latches to press the door gasket firmly against the box. The door was grooved to accommodate the door rubber gasket with a cross section of 6-mm diameter. The early effort to accommodate and mount the test PCBs in the chamber led to two designs. One was the forced-air setup in which eight test PCBs were placed equally spaced in parallel in a plastic duct through which air was sucked past the PCBs using a top-mounted blower. The other was the paddle wheel setup in which eight PCBs rotated around a central vertical axis using a top-mounted motor.

The performances of the two FOS chamber setups were analyzed in terms of copper and silver corrosion rates. The forced-air setup had higher air velocity over the test PCBs and, therefore, resulted in higher corrosion rates compared to the paddle wheel setup. The ease of use and control of the paddle wheel led to its becoming the setup of choice. The use of the forced-air setup was later abandoned.

In the early stages of the test development, sulfur vapor was the only corrosive chemical in the chamber air. The FOS chamber with only sulfur vapor and moisture failed to cause creep corrosion on PCBs from lots that had suffered creep corrosion in the field. Clearly, another corrosive gas was needed that would act synergistically with sulfur vapor. In the absence of such a gas, the synergistic role of dust comprising ammonium salts (known to exist in 2.5-µm particles in polluted geographies) was considered to reproduce the creep corrosion in the laboratory with the same morphology as observed in the field. Indeed, with the sulfur as the only corrosive chemical in the chamber, ammonium salt dust proved to be necessary to create creep corrosion. Creep corrosion was created with similar morphology as that observed in the field when the PCBs were coated with ammonium salts and exposed to sulfur and high humidity in the FOS chamber.

In the next stage of the test development, the project team considered the necessity of a gas in place of the ammonium salt dust to work synergistically with sulfur vapor. Ozone and oxides of nitrogen were obvious choices but the team could not come up with a convenient means of introducing these gases into the chamber in a controlled manner. Clorox was then explored as a source of chlorine gas that would work in synergy with sulfur. Early experiments with Clorox proved successful in causing creep corrosion with morphology very similar to that observed in the field. The problem with Clorox was that, being an aqueous solution of sodium hypochlorite, the presence of Clorox in the chamber raised the relative humidity in the chamber to near 100%. In other words, with Clorox in the chamber, humidity control was lost. The team considered various innovative techniques to control the relative humidity in the chamber in the presence of Clorox.

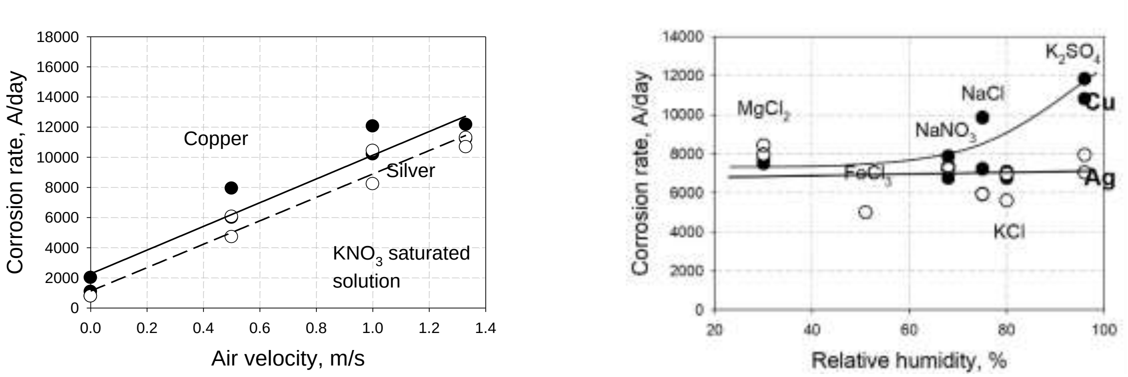
The one that proved successful consisted of a scheme that forced the water vapor from the Clorox to flow over a large-area saturated salt solution to give the saturated salt solution the dominant role to control the relative humidity in the chamber. In the latest version of the FOS chamber, the sulfur concentration and the relative humidity are well controlled and the chlorine concentration changes over time but in a somewhat reproducible manner.

Forced-air setup

The forced-air setup for mounting the test PCBs is described in **Figure 6.1**. Eight equally spaced PCBs are mounted vertically on the air inlet side of the setup. A blower on top pulls air through the setup. Air is forced to flow horizontally over the PCB surfaces, then through a U-bend followed by being pulled up by the blower. Air flow over the PCBs surfaces can achieve velocities of up to 2m/s. The humidity was controlled by saturated KCl salt solution in two 100mm diameter petri dishes. The sulfur was in two 80mm diameter petri dishes. The chamber temperature was held constant at 60°C. At this stage of the development, there was no Clorox in the chamber. The effects of air velocity and relative humidity on copper and silver corrosion rates are shown in **Figure 6.2**. Notice that the corrosion rates are a function of air velocity and that the copper corrosion rate increases with relative humidity, but the silver corrosion rate is quite independent of relative humidity. The forced-air setup, while clearly an excellent approach to studying corrosion at high air flow rates and as a function of air velocity, was put aside in favor of the paddle wheel setup whose development is described below.

Paddle wheel setup

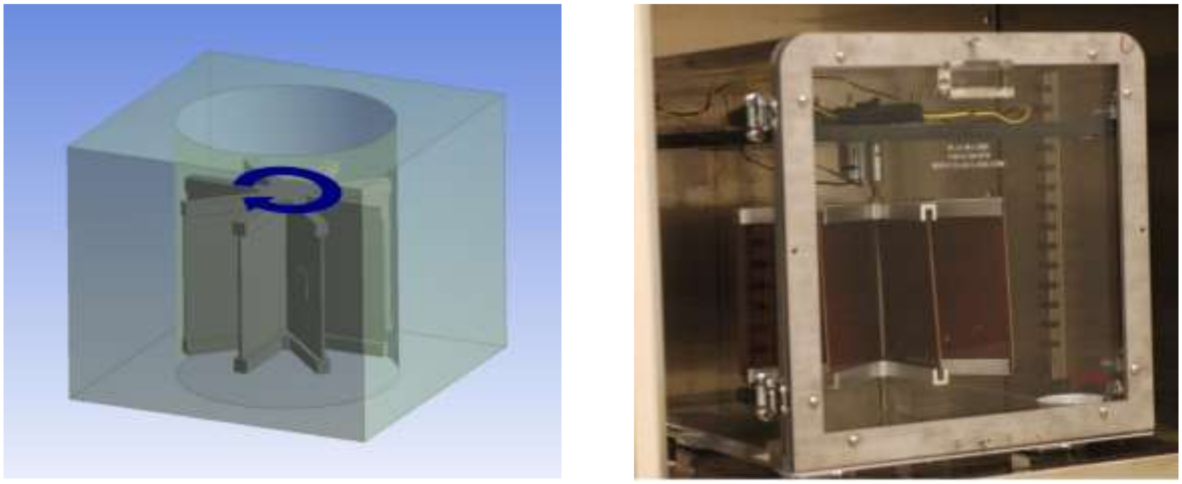
The paddle wheel setup, shown in **Figure 6.3**, was favored over the forced-air setup because of ease of control and ability to have consistent air flow conditions over the PCBs across laboratories worldwide. The one major disadvantage of the paddle wheel setup, which the team decided to accept, is that the air flow over the PCBs is limited to less than 0.1m/s. As in the forced-air setup, the paddle-wheel setup also had the saturated salt was in two 100mm diameter petri dishes and the sulfur was in two 80mm diameter petri dishes in a FOS chamber at 60°C. **Figure 6.4** shows that the temperature and humidity can reach steady state within about two hours. The copper and the silver corrosion rates are shown in **Figure 6.5.** At this stage of the test development Clorox had not been considered as a source of chlorine gas. Notice that, as in the case of the forced-air setup, the corrosion rates in the paddle wheel setup are a function of air velocity and that the copper corrosion rate increases with relative humidity, but the silver corrosion rate is quite independent of relative humidity.



(a) Relative humidity was held constant at 82% by KNO$_3$ saturated salt solution

(b) Air velocity was held constant at 1 m/s

Figure 6.2: The copper (solid circle) and silver (open circle) corrosion rates as a function of air velocity and relative humidity in forced-air setup at 60°C and 1m/s air flow. The corrosion rates were obtained by the weight gain of 25 x 50 mm metal foils.



schematic

actual setup

Figure 6.3: Paddle wheel setup

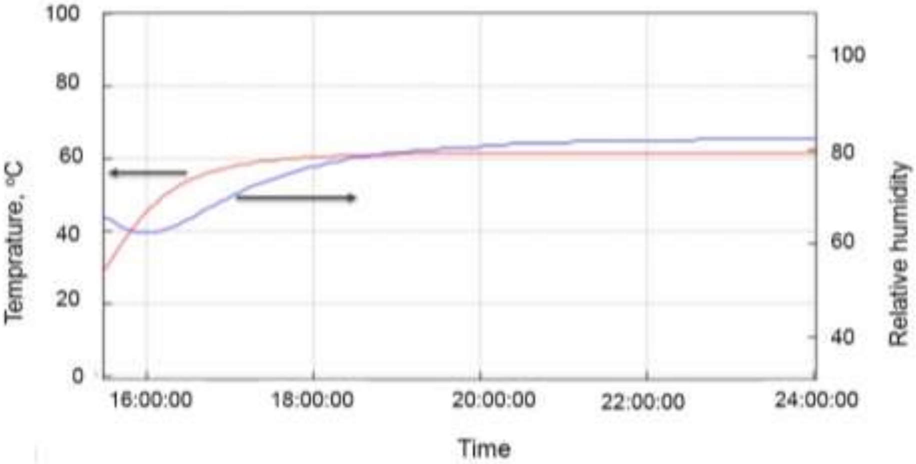
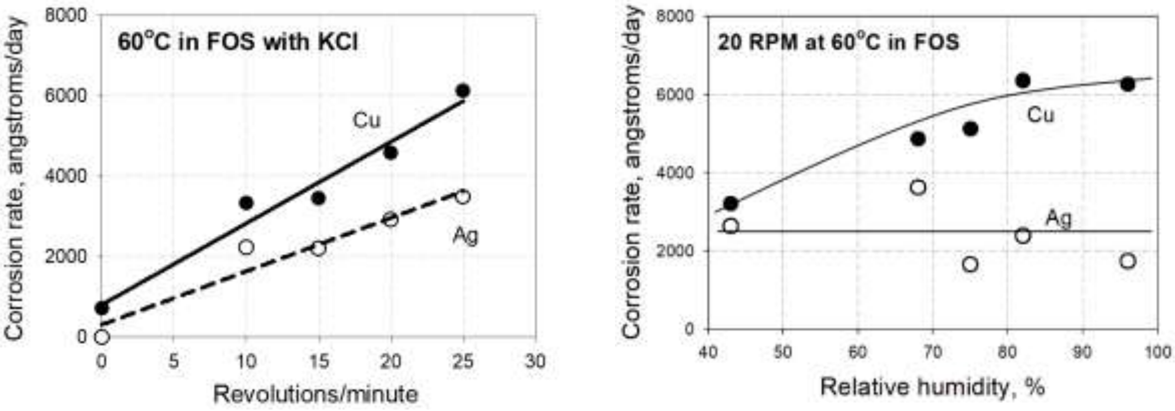


Figure 6.4: Temperature and relative humidity reach near steady state in about two hours.



80% relative humidity

Rotation speed held constant at 20 RPM

Figure 6.5: The copper (solid circle) and silver (open circle) as function of air velocity and relative humidity in paddle wheel setup at 60^{o}C and less than 0.1m/s air flow. The corrosion rates were obtained by the weight gain of 25 x 50 mm metal foils.

6.2 Role of fine dust on creep corrosion

ASHRAE published results of a survey of the quality of air associated with the occurrence of creep corrosion and the corrosion of surface mount resistors in the 2011 white paper on particulate and gaseous contamination guidelines for data centers **[26]. ** The paper concluded that for corrosion-related hardware failures to occur, the copper and silver corrosion rates must be greater than 300 and 200 angstroms/month, respectively. Though the survey did not include temperature and humidity observations, most mission critical data centers maintain the temperature and humidity well within the ASHRAE recommended limits of 18-27°C and relative humidity less than 60%. For corrosion products such as sulfides and/or for metallic ions to creep on PCB surfaces there must be an adsorbed moisture film on the surface forming an electrolytic path through which material transport can occur. Since a typical mission critical data center has well controlled and low relative humidity, for creep corrosion to occur, there must be dust with low deliquescent relative humidity settled on the PCB surface which can absorb moisture from the air and get wet even under low relative humidity conditions. It turns out that in polluted geographies, high levels of particulate contamination do occur along with the high levels of gaseous pollution.

Airborne dust in data centers can be characterized into two size ranges: coarse dust with particle size greater than 2.5 µm, and fine dust with particle size less than 2.5 µm. Coarse dust is mainly from mineral sources. It is low in ionic salts, which makes it less corrosive, and it can be very effectively kept from entering data centers by common filtration practices. Fine dust is of particular concern because the water-soluble ions represent a significantly greater fraction of its mass compared to coarse dust which has much lesser ionic content **[31]**. The source of fine dust is both anthropogenic and natural. Nitrogen dioxide from automobile exhaust, ammonia from agriculture and sulfur dioxide from coal fired power plants can combine in the atmosphere, possibly on submicron carbon particles, to produce fine particles of ammonium sulfate, ammonium hydrogen sulfate and ammonium nitrate **[32].** Of the three, ammonium hydrogen sulfate has the lowest deliquescent relative humidity (DRH) of 40% **[33]**. Depending on the composition, fine dust can have an effective DRH of 50-65% **[34]**. In contrast, the effective DRH of a typical clean metal surface is in the range 70-80% **[33]**. Fine dust on surfaces can have three detrimental effects: (1) if the relative humidity in the room is above the DRH of the dust, the dust will get wet and support corrosion; (2) the increased surface area due to the fine dust will provide additional area on which gases can be adsorbed, thus increasing the rate of corrosion of the underlying metal; and (3) dust particles can increase the rate of corrosion through differential aeration. It has been suggested that to mimic field conditions, especially those in the more polluted geographies, the qualification test for electronic devices should include both the influence of atmospheric particulate and gaseous contamination **[35]**.

Research by AT&T Bell Labs **[33]** addressed the contributions of both particulate and gaseous contamination in which a novel but complicated means of generating submicron particles was described and it was concluded that the average acceleration factor from particle deposition was 100. The effect of fine dust on electronic hardware, without any contribution from gaseous contamination, was studied by a team at the Lawrence Berkeley National Lab **[34]** using a novel means of generating fine ammonium sulfate particles and measuring the degradation of electrical surface insulation resistance as a function of relative humidity and voltage. The insulation resistance was found to decrease by several orders of magnitude with increasing relative humidity, even when the room humidity was below the DRH of the fine particles on the test circuit boards. Electrostatic forces were found to enhance the segregation of fine particles on the test circuit boards in the 50-65% humidity range. The fine dust chemical constituent of main concern is probably the ammonium hydrogen sulfate because of its low deliquescent relative humidity of 40%. The high ionic content of the settled fine particles provides the electrolytic path for the metallic ions and corrosion products to creep on the PCB surfaces. As mentioned previously, particles can also contribute to degradation of hardware reliability in two other ways: (1) particles on metal surfaces may increase the rate of metal corrosion by differential aeration induced localized corrosion and (2) by increasing the surface area for gas adsorption.

Creep corrosion testing with dust

As mentioned in the previous section, it is probable that the necessary conditions for creep corrosion in data centers, with well controlled temperature and humidity conditions, may be the high levels of gaseous and particulate contamination. The most corrosive salt in fine dust is probably ammonium hydrogen sulfate because of its low deliquescent relative humidity of 40%. Besides the obvious need for reduced sulfur, the early and expansive work by Abbott **[5]** pointed to the need for NOx and Cl_2/chlorides in the environment to enhance copper corrosion rates. In iNEMI's exploratory work, these two components were represented by ammonium salts and by NaCl in the form of dust. We covered the test PCBs with dust consisting of equal parts of $(NH_4)_2SO_4$, NH_4HSO_4, NH_4NO_3 and NaCl before subjecting them to the FoS vapors in the test chamber.

The challenge was to develop a convenient way to apply a controlled amount of the dust uniformly distributed on the test PCB surfaces prior to stressing the PCBs in the FoS chamber. The objective was to achieve 10-500 $\mu g/cm^2$ total salt concentration on the test PCB surfaces. The procedure explored to spread the dust on the PCBs was to mix a solution of 25% by mass of each of the four salts —$(NH_4)_2SO_4$, NH_4HSO_4, NH_4NO_3 and NaCl — pour a controlled amount of the aqueous solution on the test PCB and let the solution dry, leaving behind the salts on the PCB surface. Uniform distribution of salt could not be achieved because the water/PCB surface tension kept puddling the water into large droplets, thus, concentrating the salt in the areas last to dry. We failed to achieve a uniform salt distribution across the complete PCB surface. So, instead, we decided to apply small droplets of the dilute salt solution locally on areas of interest on the PCBs. By controlling the volume of the drop the wetted surface area and the salt solution concentration, the project team achieved the desired salt concentration locally by doing the following. A dilute solution of 0.125g each of $(NH_4)_2SO_4$, NH_4HSO_4, NH_4NO_3 and NaCl in 100ml de-ionized water was dropped on selected areas of a PCB using a glass pipette. Each drop was about 4mm in diameter and about 2mm high. When a droplet dried over a 4mm diameter area, it left an average total salt concentration of about 500 $\mu g/cm^2$. Since the salt contamination is applied locally on a PCB, the locations of application must be carefully noted for future reference. One advantage of this approach is that salts with many different surface concentrations can be deposited and simultaneously studied on a test PCB. For example, it is possible to deposit 10 drops of 10 different salt concentrations so that the effect of 10 different salt concentrations can be studied simultaneously on one test PCB.

The amount of salt on a surface can be determined by extracting the salt in de-ionized water and measuring the increase in the electrical conductivity of the water. The deliquescent relative humidity of a dust can be determined by covering interdigitated comb coupons (SIR test board, IPC-B24 Rev A) with the dust and applying 10 V across the combs, separated by 0.5 mm spacing, and measuring the leakage current while raising the relative humidity in a step-wise or linear manner **[36]**. The deliquescent relative humidity of this dust was somewhere between 50% and 62%.

The proof of an effective creep corrosion qualification test lies in its ability to discern between PCBs that will fail in the field and those that will not. A FoS test with a single corrosive chemical lacks the synergistic effects of various gaseous contaminants and fine dust that PCBs encounter in service. To include the effects of NOx and Cl_2/chlorides and those of ammonium-salt containing fine dust, an ImAg-finished PCB from a lot with known field history of high propensity to creep corrosion, was locally contaminated with controlled amounts of four salts ($(NH_4)_2SO_4$, NH_4HSO_4, NH_4NO_3 and NaCl) as explained in the earlier section. A

(a) No creep corrosion occurred in the absence of dust

(b) Creep corrosion in the presence of dust

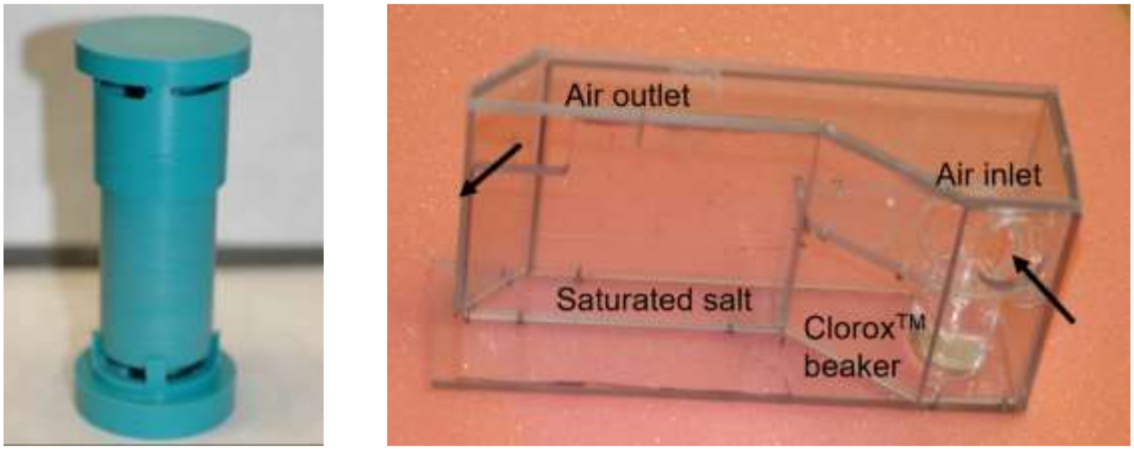
(c) Creep corrosion in the field

Figure 6.6: Effect of ammonium and NaCl containing dust on creep corrosion in FoS chamber with sulfur and high humidity.

PCB from the same lot, used as a control card, was not contaminated with the dust. The two PCBs were subjected to FoS vapors at 60°C, 82% relative humidity using KNO_3 saturated salt solution, and 1m/s air velocity. After three days of stressing, the PCBs were optically examined at low magnification. **Figure 6.6a** shows the non-contaminated PCB to have heavy corrosion of the copper pads, but no creep corrosion. **Figure 6.6b** shows extensive creep corrosion in the local areas contaminated with the ammonium and NaCl salts. The morphology of this creep corrosion is somewhat like that seen on the failed cards returned from the field (**Figure 6.6c**).

6.3 Introduction of chlorine gas

There was a clear need for the introduction of a gas that could act in synergy with sulfur and moisture to cause creep corrosion on susceptible PCBs. The FoS chamber is a closed chamber with no gas flowing in and/or out. In a MFG chamber air flows in and out of the chamber. The gases and moisture stay in the FoS chamber for the duration of the test. Ozone and nitrous oxide were considered but no easy, convenient way was found to introduce these gases into the chamber. Next, the team turned its attention to chlorine gas. The idea of chemically generating chlorine gas was considered and discarded. We then explored the use of Clorox, a household bleach, which is an aqueous solution of sodium hypochlorite. FoS test runs with 100ml Clorox in a beaker with the inside lined with paper napkins proved very successful in reproducing creep corrosion on PCBs from lots that had suffered creep corrosion in the field. Note that, as earlier mentioned, we had not been able to reproduce creep corrosion on these PCBs without the introduction of ammonium salts or Clorox. The idea of lining the inside of the Clorox containing beaker with paper napkins came from a test developed at IBM Austin by Janet Rice for testing gold-plated electrical contacts for porosity. It is speculated that the paper napkins may cause early quick release of the chlorine gas. We abandoned the use of paper napkins in later tests. At this point in the development effort, we realized that since Clorox is a dilute, aqueous solution of sodium hypochlorite, the saturated salt in the chamber cannot dominate and control the relative humidity in the chamber. In the presence of Clorox, the humidity in the chamber would rise to near saturation and therefore could not be controlled.



Solution 1: Vertical arrangement of chemicals

Solution 2: Blower-driven arrangement

Figure 6.7: Potential solutions that would let Clorox release chlorine gas without upsetting the relative humidity in the chamber.

The challenge of having the Clorox release chlorine gas into the chamber but not upset the relative humidity in the chamber led to extensive innovative effort. The first idea considered was that of a vertical arrangement of chemicals as shown in **Figure 6.7a** in which the moisture and chlorine coming off the Clorox are made to flow over a saturated salt solution purely by convection and diffusion. A prototype setup was fabricated but did not prove successful. The second idea, shown in **Figure 6.7b**, was to blow air over a Clorox containing beaker and then over a saturated salt solution bath. This second idea was also unsuccessful and abandoned.

The idea that proved successful was to arrange the chemicals horizontally so that diffusion and convection would allow chlorine from the Clorox to make its way out of the setup but force the water vapor coming out of the Clorox to equilibrate with the saturated salt solution. This setup to control the sulfur and chlorine gas concentrations and the relative humidity in the chamber is described in **Figure 6.8**. The sulfur is contained in a 275mm square tray, 20mm deep, with a 195mm circular opening in the center. The sulfur concentration is controlled by placing the chamber in an oven maintained at a constant 50°C. The household bleach, containing 8.25% sodium hypochlorite, is contained in a 145mm diameter petri dish that sits inside the sulfur tray on the same platform as the sulfur tray. The saturated salt solution is in a 190mm diameter tray with a circular opening of 65mm diameter in the center, which is covered by a circular plate with 1mm or 3mm setup gap to allow controlled escape of the chlorine gas from the bleach. The cover plate also throttles the escape of water vapor from the bleach such that the saturated salt solution can dominate the relative humidity in the chamber at its deliquescence relative humidity. The setup is able to control the temperature and relative humidity at the desired values. The chamber reaches steady state in two hours. Humidity control, in the presence of Clorox, is most challenging to achieve in the low humidity range because of the water vapor given off by the household bleach which is also the source of the chlorine gas. The proof that the setup overcame this challenge is demonstrated by zinc chloride saturated solution in the chamber controlling the humidity at about 11%, which is the deliquescence relative humidity of $ZnCl_2$.

With the horizontal setup, the relative humidity in the chamber can be controlled to almost any value in the 11-90% range by using a salt that has its deliquescence relative humidity equal to or near the desired relative humidity value. The ability to have a chamber with sulfur and chlorine gases and to be able to achieve any desired relative humidity in a wide range opens the possibility of measuring copper and silver corrosion rates and the occurrence of creep corrosion as a function of relative humidity.

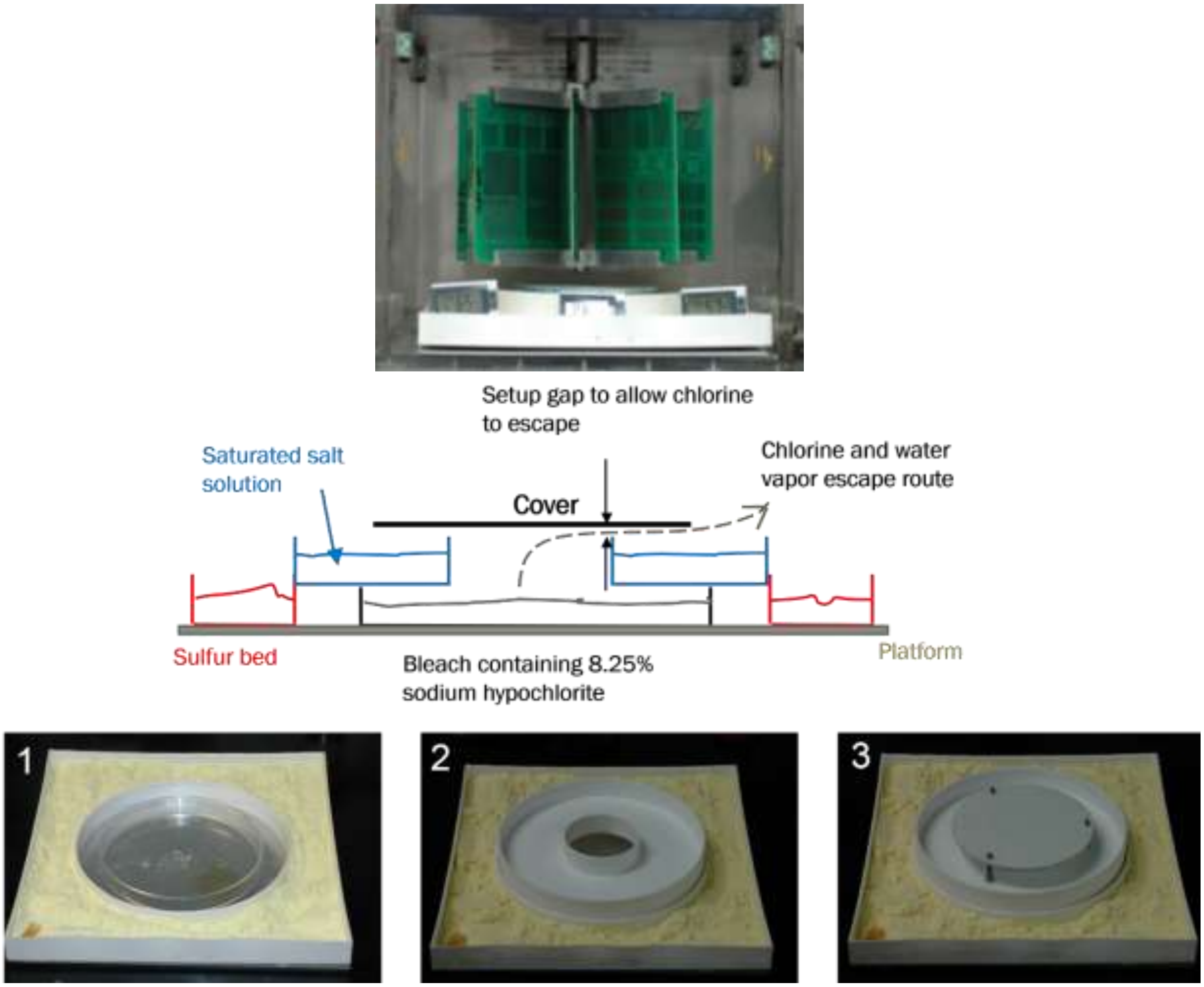
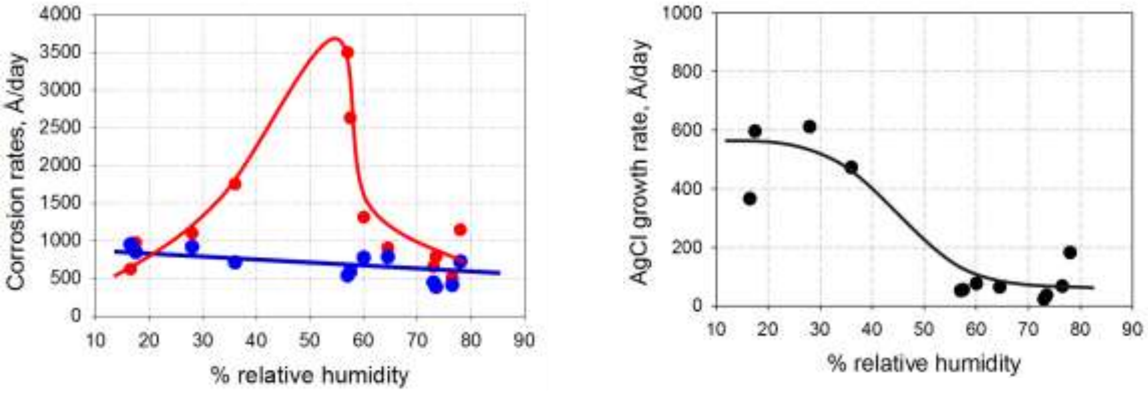


Figure 6.8: Bleach setup in cross section and in pictorial format.

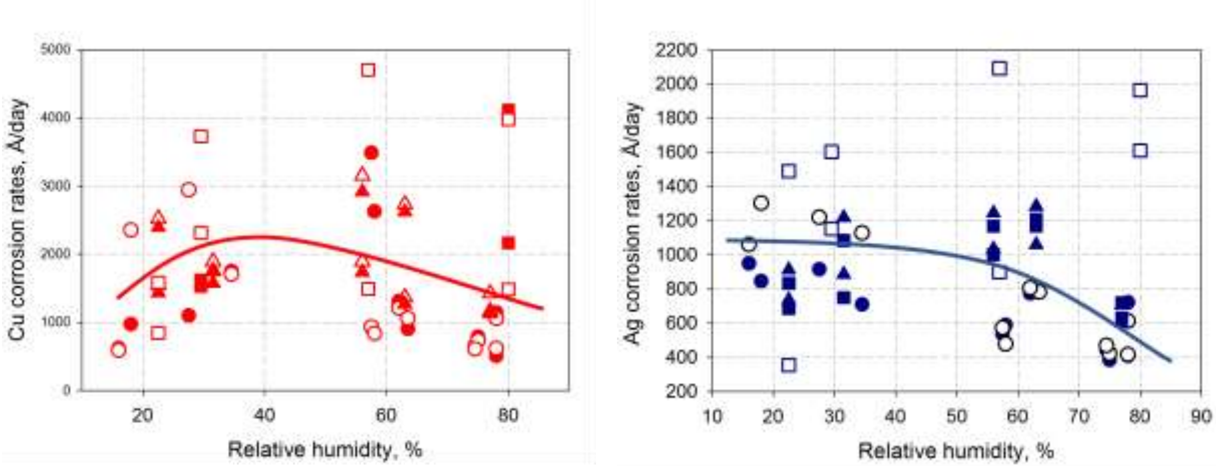
Copper and silver corrosion rates in two independent test runs are shown in **Figures 6.9** and **6.10**. The silver corrosion rates in iNEMI FoS chambers decrease somewhat with increasing relative humidity as shown in **Figure 6.9a** and **6.10b**. The AgCl formation rates decrease somewhat dramatically with increasing relative humidity as shown in **Figure 6.9b**. These observations lend support to the hypothesis that chlorine concentration decreases with increasing relative humidity. At high relative humidity, the



(a) Cu (red) and Ag (blue) corrosion rates.

(b) AgCl formation rate.

Figure 6.9: Corrosion rates in FoS chamber loaded with six test PCBs and one set of 25 x 50mm copper and silver foils.

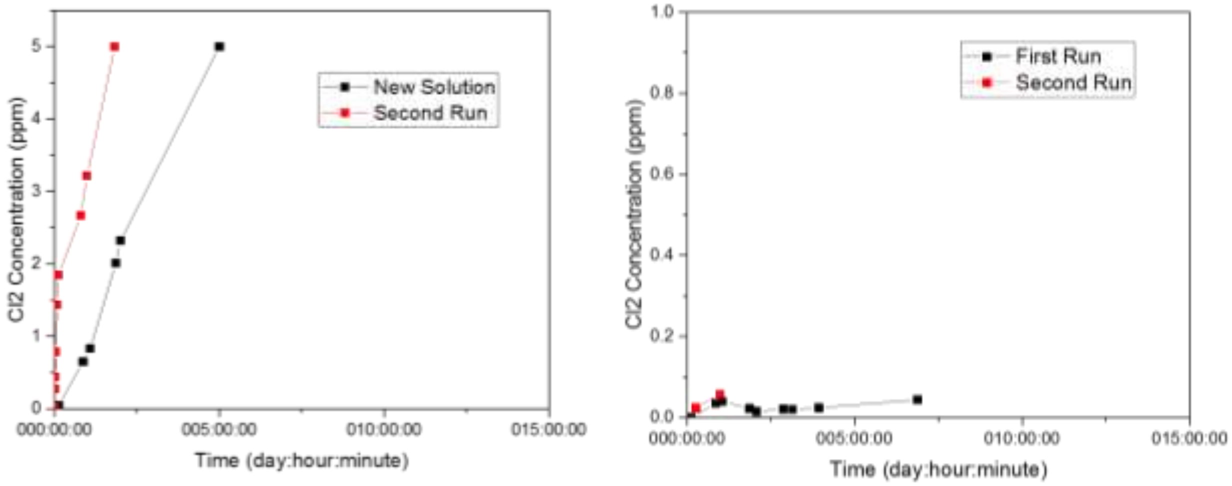


(a) (b)

Figure 6.10: Another example of copper and silver corrosion rates with the same conditions as in Figure 6.9.

chamber walls absorb more moisture which in turn absorbs more chlorine from the atmosphere. This hypothesis is proven by comparing **Figures 6.11a** and **6.11b**. At low humidity (**Figure 6.11a**) the chlorine concentration in the chamber is high, and at high humidity (**Figure 6.11b**) the chlorine concentration is low. Also notice that in **Figure 6.11a**, the chlorine concentration is less in the second run compared to the first run. This is probably because the chamber walls became saturated with absorbed chlorine gas during the first run.

The behavior of copper corrosion as a function of relative humidity, shown in **Figures 6.9** and **6.10**, is interesting. As would be expected, the copper corrosion rate increased with increasing humidity in the low relative humidity range **[37, 38]**. (Increased humidity typically increases corrosion.) However, the copper corrosion rate was found to decrease with increasing humidity in the high relative humidity range. This result is most likely due to the adsorption of the chlorine gas by the higher levels of moisture adsorbed on the chamber walls, decreasing the chlorine concentration in the chamber. This is probably the first time such behavior has been reported.



$ZnCl_2$ saturated salt solution (13-19%RH) KCl saturated salt solution (74-80%RH)

Figure 6.11: The concentration of chlorine gas in the FOS chamber coming off the household bleach is a strong function of the humidity in the chamber. With $ZnCl_2$ saturated salt solution, the humidity in the chamber is 13-19% and the Cl_2 concentration is in the ppm range; whereas, with KCl saturated salt solution, the humidity in the chamber is 74-80% and the Cl_2 concentration is in the tens of ppb range.

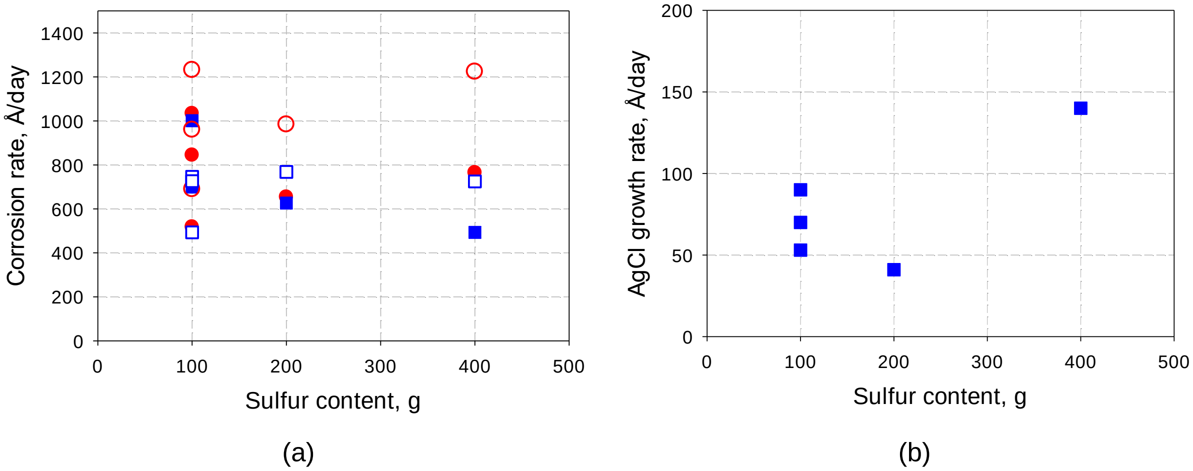


Figure 6.12: The effect of the amount of sulfur in the chamber on copper and silver corrosion rates.

The role of the amount of sulfur in the chamber on copper and silver corrosion rates is shown in **Figure 6.12a**. As expected by thermodynamic reasoning, the amount of sulfur in the chamber has little effect on the metal corrosion rates, though the amount of sulfur would influence the kinetics (i.e., the rate at which the sulfur vapor concentration approaches the thermodynamic equilibrium). **Figure 6.12b** shows that the AgCl formation rate is also little effected by the amount of sulfur in the chamber.

Chlorine concentration control is a challenge. We measured chlorine concentration in the air indirectly by measuring the AgCl growth rate on silver foils. There is much variability in the rate of formation of AgCl during the test runs most probably due to variability of the household bleach chemistry. Another source of variability may be variations in the synergistic effects of chlorine, sulfur and moisture in the air on the AgCl growth rate. We decided to study the role of household bleach dilution on the chlorine concentration as measured by the AgCl growth rate during five-day test runs. The results are summarized in **Table 6.1**. One surprising result is that dilution of the household bleach by 50% did not decrease the rate of copper and silver corrosion. Work continues to improve the means of controlling the chlorine concentration in the chamber.

The iNEMI FoS test chamber is shown in **Figure 6.13**. This figure shows a typical oven in which the chamber is placed to heat the chamber to a uniform 50°C, along with a fully loaded chamber with and without the front cover of the chamber.

Table 6.1: Copper and silver corrosion rates as a function of bleach dilution

Run #	%RH	Bleach concentration*	Bleach pH	Corrosion rates by coulometric reduction, Å/day			Corrosion rates by mass gain, Å/day	
				Cu total	Ag total	AgCl	Cu total	Ag total
C5	60-63	100%	10.8	769	668	59	928	739
C7	58-61	50%	10.8	1350	1058	53	1170	925
C8	58-59	100%	10.8	930	1296	21	1197	1058
C9	58-59	50%	10.8	1482	1349	30	1697	2590

* 100% means no dilution. 50% means 1 part of water added to one part of bleach. All test runs except for the C9 run were for five days. The C9 run was for one day.

(a) Oven (b) Chamber in oven (c) Chamber, front door removed

Figure 6.13: iNEMI FOS chamber with paddle wheel setup.

7. Effect of PCB loading and the role of PCB prebake

7.1 Effect of loading

The effect of loading the chamber with PCBs was studied. Each test run had a total of eight circuit boards. One of the eight circuit boards had 25x54mm copper and silver foils mounted on it. The circuit boards called “green sheets” in **Figure 7.1** are the test circuit boards. Test runs were made with zero, four, six and eight of these green sheets. The remaining slots were filled with brown boards. The brown boards were epoxy boards that we found did not absorb sulfur. Each run had a total combined number of eight green and brown boards. Notice that as the number of green sheets increased, the copper and silver corrosion rates decreased. This decrease in corrosion rate as a function of loading with green sheets could be due to the increased absorption of the sulfur vapors by the green sheets, decreasing the sulfur concentration in the chamber air. When the sulfur surface area was increased to cover most to the chamber base, the copper and silver corrosion rates increased dramatically. The need for a large-surface-area sulfur bed became evident. Subsequent test runs had the maximum surface area of sulfur permitted by the chamber size.

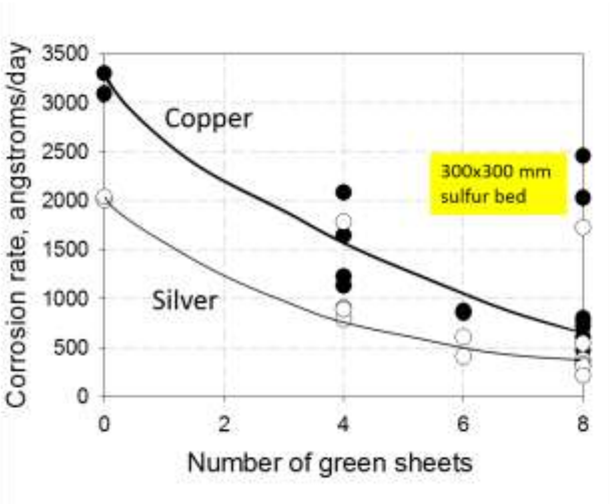
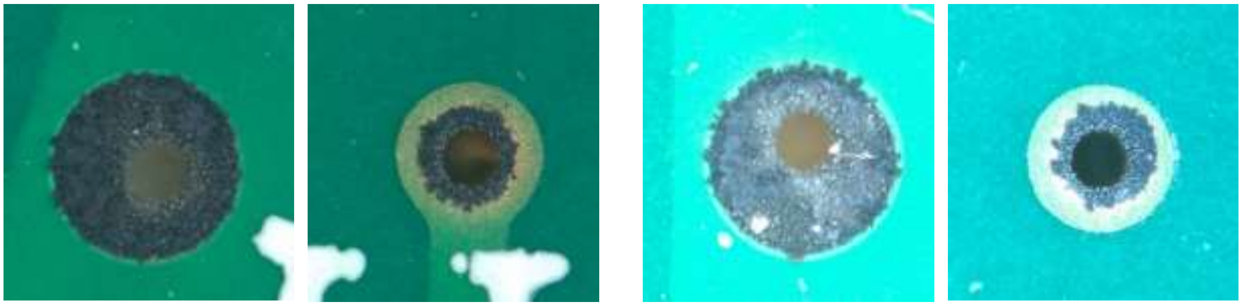
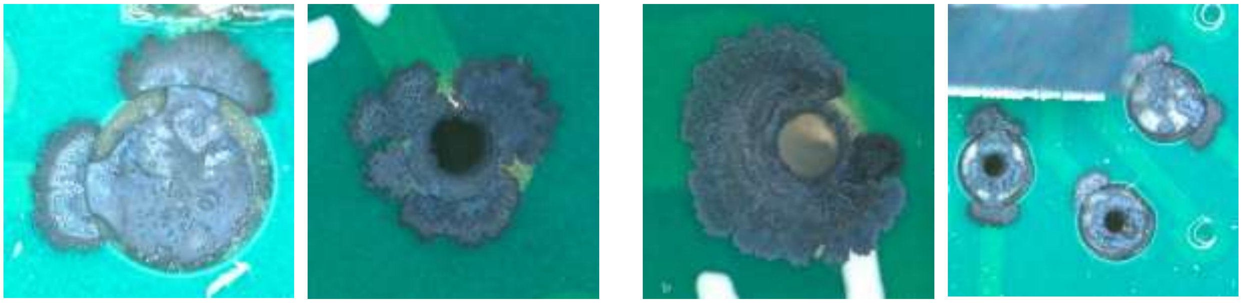


Figure 7.1: Effect of loading: The total sum of the green and brown epoxy boards was kept constant at eight in each of the runs. E.g., when the number of green sheets was four, the number of brown epoxy sheets was three. The 8th slot on the paddle wheel was occupied by a sheet on which copper and silver foils were mounted for corrosion rate measurements. The sulfur was in two petri dishes. When the sulfur bed was raised to 300x300mm area, the corrosion rates increased dramatically. **[39]**



Unbaked card A

Unbaked card B



Pre-baked card C

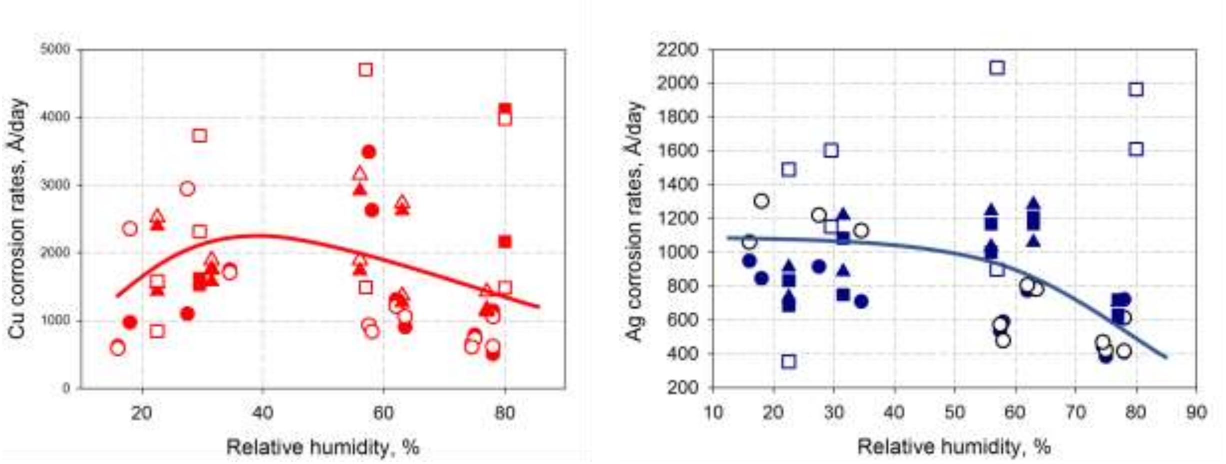
Prebaked card D

Figure 7.2: Demonstration of the role of pre-baking the PCBs. The four PCBs in this test were from a lot that suffered creep corrosion in the field. Cards A and B, which were not pre-baked, did not suffer creep corrosion in the iNEMI FOS test chamber; whereas cards C and D, which were pre-baked, suffered creep corrosion in the test. Two examples of corrosion are shown for each card. **[40]**

7.2 Pre-baking the PCBs

The role of pre-bake was studied using PCBs from a production lot that suffered creep corrosion in the field. The prebake consisted of pre-baking at 100°C in flowing nitrogen gas for 24 hours to possibly rid the PCBs of much of their volatile organic compounds. Pre-baking was done in a desiccator in which the PCBs are placed equally spaced in parallel or radially. The desiccator was loosely covered with aluminum foil. The end of the copper tube used for the nitrogen gas was inserted into the desiccator so that the flowing gas could flush away the VOCs from the boards. The copper tube should have many coils inside the oven so that when the gas exits into the desiccator it is heated to 100°C. Two PCBs (A and B) that were not pre-baked and two that were pre-baked (C and D) were tested using the 20 rpm paddle wheel setup in a flowers-of-sulfur chamber at 50°C that included 40ml Clorox in a 100ml beaker. **Figure 7.2** shows the results. The PCBs that were not pre-baked did not suffer creep corrosion; whereas, the pre-baked PCBs suffered creep corrosion with morphology similar to that experienced in the field.

In the early phase of the iNEMI project, the team recognized that the loading of the FOS chambers with iNEMI test vehicles lowered the corrosion rates of copper and silver as shown in **Figure 7.1**. Clearly, the PCBs were affecting the chamber environment, making it less corrosive to copper and silver. The sulfur concentration level in the environment could be possibly depleted by absorption of the sulfur by the PCBs, or the PCBs could be giving off volatile compounds that could be coating and thus protecting the copper and silver foils from corrosion. It is not clear by what mechanism PCB loading affects the corrosivity of the environment. If there are volatiles coming off the PCBs they would, over time, build up in the chamber and, therefore, must be removed to avoid contaminating the chamber. It was this consideration of avoiding the buildup of volatile contamination coming off the PCBs that led to the decision to study the effect of pre-baking on creep corrosion. Testing has consistently shown that pre-baking promotes creep corrosion on



(a) Cu corrosion rates (b) Ag corrosion rates

Figure 8.1: Corrosion rates in FoS chamber loaded with six test PCBs and one set of 25 x 50mm copper and silver foils. (This is the same as Figure 6.10.)

PCBs. PCBs of multiple part numbers and different manufacturers from production lots known to have suffered creep corrosion in the field have proven that pre-baking is necessary to produce creep corrosion similar in morphology to that experienced in the field.

8. Round-robin testing of the effect of relative humidity on creep corrosion

The objective of this round-robin testing **[41]** was to determine the effect of relative humidity on creep corrosion and to see if the effect was similar across the three companies participating in the testing. PCBs with three finishes (ImAg, ENIG and OSP) soldered using two fluxes (OR an RO) were tested at six relative humidity levels in the 15-80% range. As per the standardized iNEMI creep corrosion test procedure **[25, 41, 42]**, the test PCBs were prebaked at 100°C in flowing nitrogen gas for 24 hours. The PCBs were subjected to two five-day exposures in the FoS chamber. Each test run had six test PCBs and one set of copper and silver foils, 25x50mm, for corrosion rate measurements using mass gain and coulometric reduction methods **[30]**. The copper and silver corrosion rates are plotted in **Figure 8.1**. The AgCl formation rate is plotted in **Figure 8.2.** The curves in these figures run average at each relative humidity

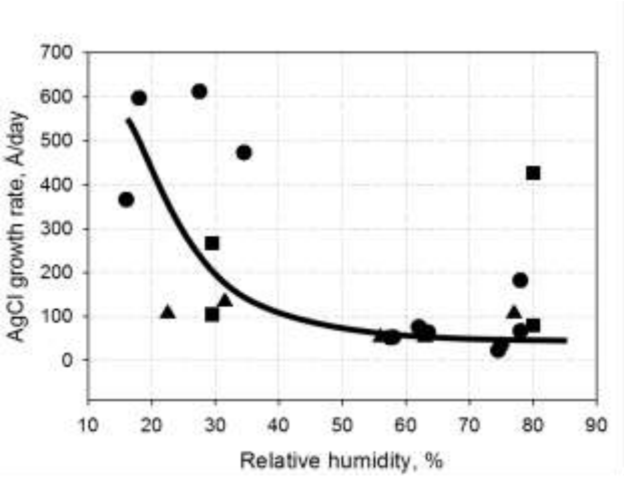


Figure 8.2: AgCl formation rates in FoS chamber loaded with six test PCBs and one set of 25 x 50mm copper and silver foils.

Table 8.1: Severity of creep corrosion after 10 days in FOS chamber at 50^{o}C, with 100ml household bleach, 1mm setup gap and paddle wheel rotating at 20 rpm

Saturated salt solutions and RH%			$ZnCl_2$ 13-30%		$MgCl_2$ 27-35%		$NaNO_2$ 55-59%		NH_4NO_3 52-68%		NaCl 69-77%		KCl 74-80%	
% of creep sites with creep corrosion			**HC**	**LC**	**HC**	**LC**	**HC**	**LC**	**HC**	**LC**	**HC**	**LC**	**HC**	**LC**
A	**ImAg**	**OR**	9	2	13	0	1	9	0	0	0	0	0	1
B			13	0	3	5	-	-	0	5	-	-	6	7
C			9	5	0	0	-	-	0	0	0	0	0	0
A		**RO**	9	2	12	1	2	9	0	0	0	0	0	1
B			-	-	5	4	-	-	4	2	-	-	-	-
C			10	5	0	0	-	-	0	1	0	0	0	0
A	**ENIG**	**OR**	0	0	12	1	0	0	0	8	0	0	3	1
B			2	3	10	4	-	-	10	3	-	-	7	7
C			0	0	0	2	-	-	0	9	0	6	3	6
A		**RO**	0	0	12	1	0	0	0	8	0	4	5	2
B			-	-	7	6	-	-	9	4	-	-	-	-
C			3	1	2	4	-	-	3	8	1	4	1	8
A	**OSP**	**OR**	0	0	2	3	0	0	0	0	0	0	0	0
B			5	5	0	3	-	-	0	0	-	-	0	0
C			3	1	0	0	-	-	0	0	0	0	1	0
A		**RO**	0	0	3	4	0	0	0	0	0	0	0	0
B			-	-	0	2	-	-	0	1	-	-	-	-
C			1	8	0	1	-	-	0	0	0	0	0	0

value — i.e., the curves are fitted through data points that are the arithmetic average of all the readings at that relative humidity. Notice that the copper corrosion rate increases with relative humidity as one would expect, but only does so in the low relative humidity range. In the high humidity range, the copper corrosion rate decreases with humidity, probably due to the chlorine gas being adsorbed on the moisture-laden surfaces. The silver corrosion rate and the AgCl formation rate decrease with relative humidity, lending support to the hypothesis that chlorine gas gets adsorbed on surfaces with adsorbed moisture, further confirmed by the direct Cl_2 concentration measurement in the chamber (see **Figure 6.11**).

Table 8.1 lists the 10-day creep corrosion results under the six relative humidity levels from 15-80%. Creep corrosion was classified as heavy creep corrosion (HC) when the corrosion products crept extensively across the PCBs, and as light creep corrosion (LC) when the distances over which the corrosion crept was very limited. The table lists the number of occurrences of HC and LC on each of the test cards. For example, the corrosion severity for an ImAg-finished card soldered using OR flux tested by Company A is listed as HC=9 and LC=2, meaning that nine of the 15 sites on the test PCB suffered heavy creep corrosion and two suffered light creep corrosion. The shaded boxes in the table indicate that the corresponding test PCBs failed the FoS test for creep corrosion.

The creep corrosion propensities of ImAg-, ENIG- and OSP-finished iNEMI test PCBs soldered with OR and RO fluxes are listed in **Table 8.1** as a function of relative humidity. The worst occurrence of creep corrosion on each of the test PCBs are presented in **Tables 8.2a-f**. Taken together these tables show that ImAg-finished boards suffer creep corrosion mostly in the low relative humidity range, below about 60%; the ENIG-finished boards suffer relatively similar creep corrosion at all humidity levels, above about 30%; and the OSP-finished PCBs suffer limited creep corrosion mostly confined to the low relative humidity range, below about 40%. These observations reported **previously [25]** are in general agreement with two earlier papers from the same project participants **[41, 42]**. In these two earlier publications, creep corrosion on ImAg-finished PCBs was confined to the lower relative humidity range, in agreement with the present observations listed in **Tables 8.1** and **8.2**. In the first of the two earlier publications, ENIG-finished PCBs suffered creep corrosion at all relative humidity levels above about 30%, in agreement with the present

Table 8.2: Worst case creep corrosion results shown as a function of relative humidity

Table 8.2a. 10-day FOS testing of ImAg-finished PCBs soldered with OR flux

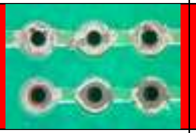
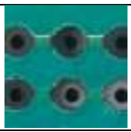
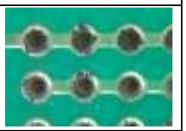
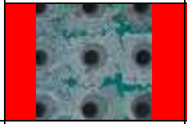
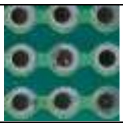
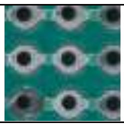
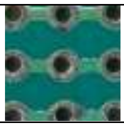
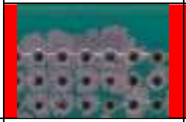
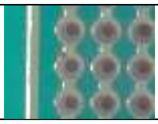
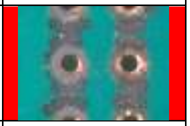
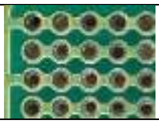
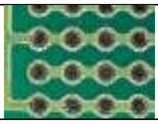
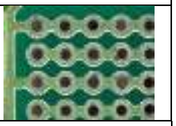
A	Batch 1	11-17% RH	31-46% RH	57-62% RH		74-77% RH	78-81% RH
					--		
	Batch 2	13-19% RH	27-37% RH	55-59% RH	56-68% RH	69-77% RH	74-80% RH
							
B	Batch 1	15-30% RH	28-35% RH		52-60% RH		74-80% RH
				--		--	
C	Batch 2	15-30% RH	28-35% RH		52-60% RH	69-77% RH	74-80% RH
				--			

Table 8.2b. 10-day FOS testing of ImAg-finished PCBs soldered with RO flux

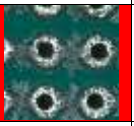
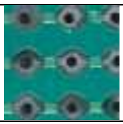
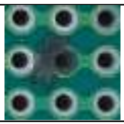
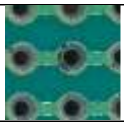
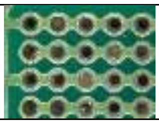
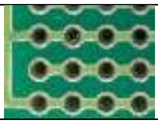
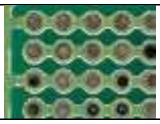
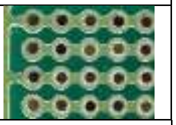
A	Batch 2	13-19% RH	27-37% RH	55-59% RH	56-68% RH	69-77% RH	74-80% RH
							
B	Batch 2		28-35% RH		52-60% RH		
		--		--		--	--
C	Batch 2	15-30% RH	28-35% RH		52-60% RH	69-77% RH	74-80% RH
				--			

Table 8.2c. 10-day FOS testing of ENIG-finished PCBs soldered with OR flux

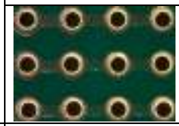
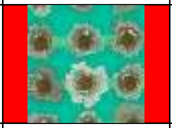
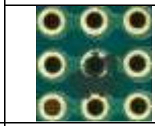
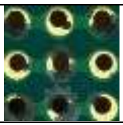
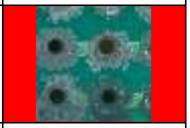
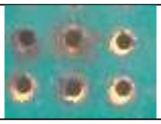
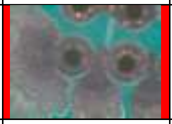
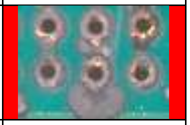
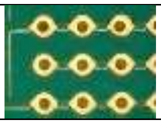
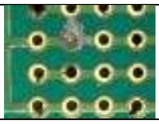
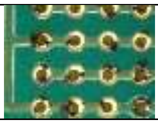
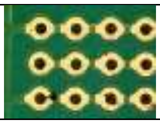
A	Batch 1	11-17% RH	31-46% RH	57-62% RH		74-77% RH	78-81% RH
					--		
	Batch 2	13-19% RH	27-37% RH	55-59% RH	56-68% RH	69-77% RH	74-80% RH
							
B	Batch 1	15-30% RH	28-35% RH		52-60% RH		74-80% RH
				--		--	
C	Batch 1	15-30% RH	28-35% RH		52-60% RH	69-77% RH	74-80% RH
				--			

Table 8.2d: 10-day FOS testing of ENIG-finished PCBs soldered with OR flux

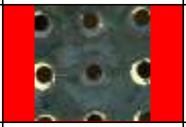
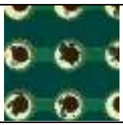
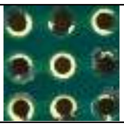
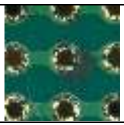
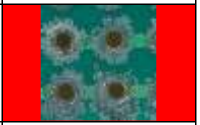
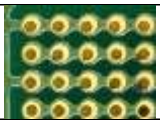
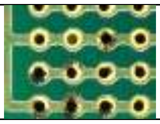
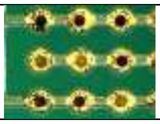
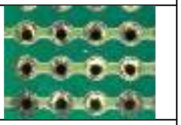
		13-19% RH	27-37% RH	55-59% RH	56-68% RH	69-77% RH	74-80% RH
A	Batch 2						
			28-35% RH		52-60% RH		
B	Batch 2	--		--		--	--
		15-30% RH	28-35% RH		52-60% RH	69-77% RH	74-80% RH
C	Batch 2			--			

Table 8.2e: 10-day FOS testing of OSP-finished PCBs soldered with OR flux

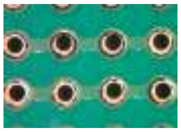
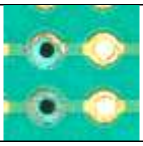
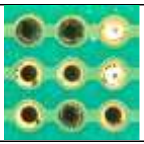
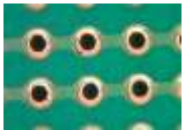
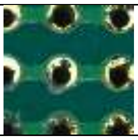
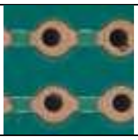
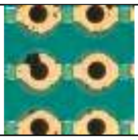
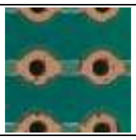
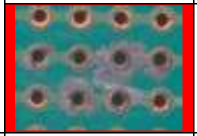
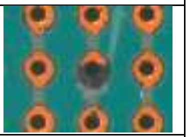
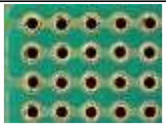
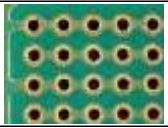
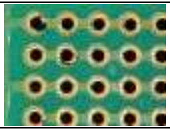
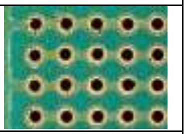
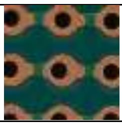
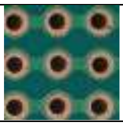
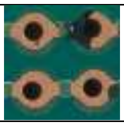
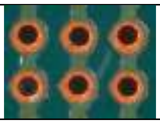
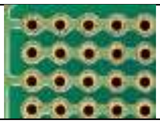
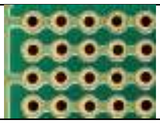
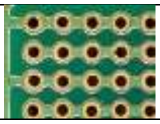
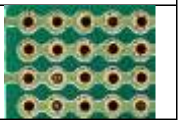
		11-17% RH	31-46% RH	57-62% RH		74-77% RH	78-81% RH
A	Batch 1		No corrosion		--		
		13-19% RH	27-37% RH	55-59% RH	56-68% RH	69-77% RH	74-80% RH
	Batch 2						
		15-30% RH	28-35% RH		52-60% RH		74-80% RH
B	Batch 1			--		--	
		15-30% RH	28-35% RH		52-60% RH	69-77% RH	74-80% RH
C	Batch 2			--			

Table 8.2f: 10-day FOS testing of OSP-finished PCBs soldered with RO flux

		13-19% RH	27-37% RH	55-59% RH	56-68% RH	69-77% RH	74-80% RH
A	Batch 2						
			28-35% RH		52-60% RH		
B	Batch 1	--		--		--	--
		15-30% RH	28-35% RH		52-60% RH	69-77% RH	74-80% RH
C	Batch 1			--			

work, but the second of the two earlier publications showed creep corrosion on ENIG-finished boards occurring only at relative humidity levels above about 70%. The earlier publications are in agreement with the OSP-finished PCBs suffering limited creep corrosion in the low humidity range less than about 40%. Overall, these works on the effect of relative humidity on creep corrosion are quite in agreement with each other.

The net of this information is that since electronic assemblies may contain PCBs finished with a range of different finishes, data center administrators cannot solely use relative humidity control to eliminate creep corrosion on the PCBs in their IT equipment. The air entering the data center must be gas-phase filtered to filter out the sulfur-bearing gaseous contamination that is responsible for creep corrosion.

It should be noted that chlorine gas concentration dramatically decreases with rising relative humidity. It is not clear what role chlorine concentration plays in the dependence of creep corrosion on relative humidity observed in this work. More work needs to be done to clarify the role of chlorine concentration on affecting the influence relative humidity has on creep corrosion.

9. Round-robin testing of the iNEMI FoS creep corrosion qualification test

The objective of this round-robin testing was to determine the reproducibility of the iNEMI FoS creep corrosion qualification test. The important test conditions were the relative humidity level and the concentration of gases such as sulfur and chlorine in the iNEMI FoS chamber. The iNEMI FoS chamber test setup and the test vehicles used are as described in earlier sections**.** Printed circuit boards with three different finishes, ImAg, ENIG and OSP, soldered with two different fluxes, OR and RO, were included in the two rounds of tests.

9.1 First round-robin test [24]

The test PCBs were pre-baked at 100°C in flowing nitrogen gas for 24 hours to eliminate the VOCs. The iNEMI FoS) creep corrosion qualification test method consists of three five-day test runs, each at a different relative humidity level.

During the first round-robin test, the first five-day test runs were at 31% relative humidity using $MgCl_2$ saturated salt solution; the second five-day runs were at 47% relative humidity using NH_4NO_3 saturated salt solution; and the third five-day runs were at 81% relative humidity using KCl saturated salt solution. In each of the three five-day test runs, the chamber reached steady state in a few hours. The 15-day iNEMI tests run thus tested for creep corrosion over a range of relative humidity levels expected in service.

Each of the six types of PCBs occupied one slot of the paddles on the paddlewheel. The other two slots were loaded with silver and copper foils on the dummy boards to monitor the corrosion rates. All three companies participating in the test used the PCBs from the same manufacturing lot.

There were differences in the results that might be explained by the differences in the test runs at the three companies, which were as follows:

- Clorox setup: All tests, but one, were run with 1-mm setup gap to throttle the outflow of moisture from the household bleach and to ensure that enough chlorine gas entered the FoS chamber. The one exception was the 3mm gap by Company B for the KCl test run.
- Test boards: Company B used new test boards for each five-day test run. Companies A and C used the same boards for all three five-day test runs.
- Amount of sulfur in chamber: Company A used ~300g sulfur, Company B used ~800g, Company C used ~180g.
- Company C used a different Clorox bleach product from Companies A and B. This resulted in a much lower AgCl formation rate at Company C.

Table 9.1: Relative humidity and corrosion rates in the three five-day test runs at the three companies (A, B and C)

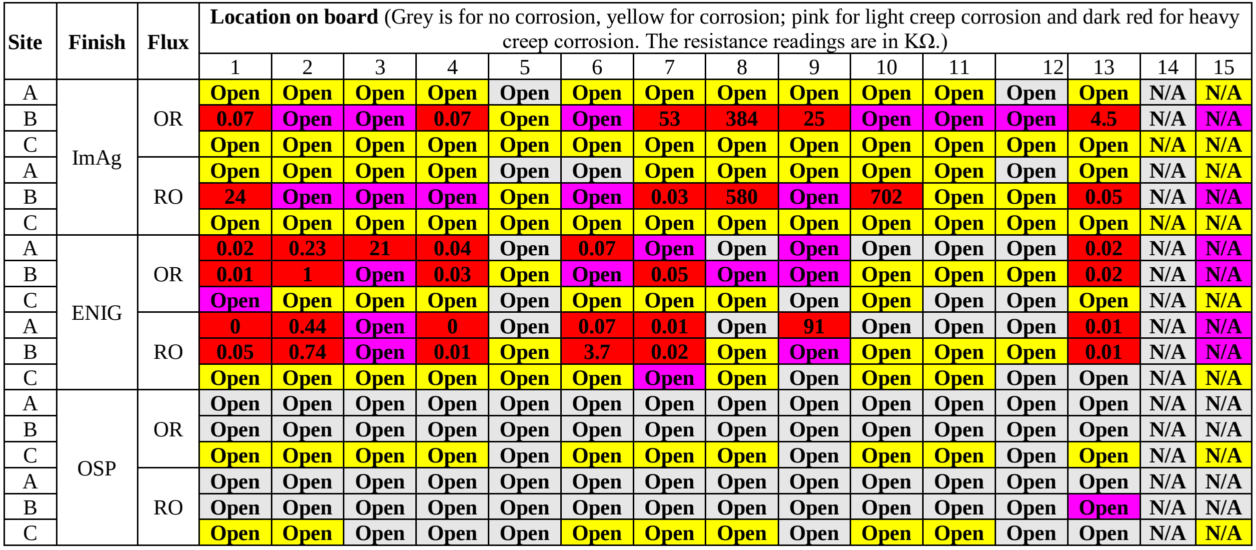
Site	Saturated salt	Bleach setup gap	Relative humidity	Cu corrosion rate, Å/day, coul reduction/mass gain	Ag corrosion rate, Å/day, coul reduction/mass gain	AgCl formation rate, Å/day, coul reduction
A	$MgCl_2$	1 mm	31-45	1667/1797	1244/1561	566
B		1 mm	38-42	1650/6591	1707/3455	598
C		1 mm	38-42	1544/--	1017/--	27
A	NH_4NO_3	1 mm	46-57	604/904	558/719	40
B		1 mm	50-51	4105/2545	1236/3428	841
C		1 mm	51-53	1386/--	1111/--	16
A	KCl	1 mm	61-78	687/--	376/--	17
B		3 mm	73-75	1603/3178	882/2720	176
C		1 mm	72-73	1369/--	704/--	16

The copper and silver corrosion rates and the rates of formation of AgCl measured during each five-day period using the coulometric reduction and the mass gain methods are listed in **Table 9.1**. The table also lists the relative humidity conditions. The extent of creep corrosion was documented after each five-day run. **Tables 9.2a-c** list the creep corrosion results for the three participating companies after each five-day test run for each of the six types of PCBs under test. **Table 9.3** shows the worst-case creep corrosion, after the three five-day tests, on the six types of PCBs tested by Company A.

The relative humidity level was well controlled by design. The saturated salt solution had the dominant role in controlling the relative humidity. The variability in the humidity levels listed in **Table 9.1** is probably more due to the accuracy of the relative humidity sensors than the actual variation in humidity.

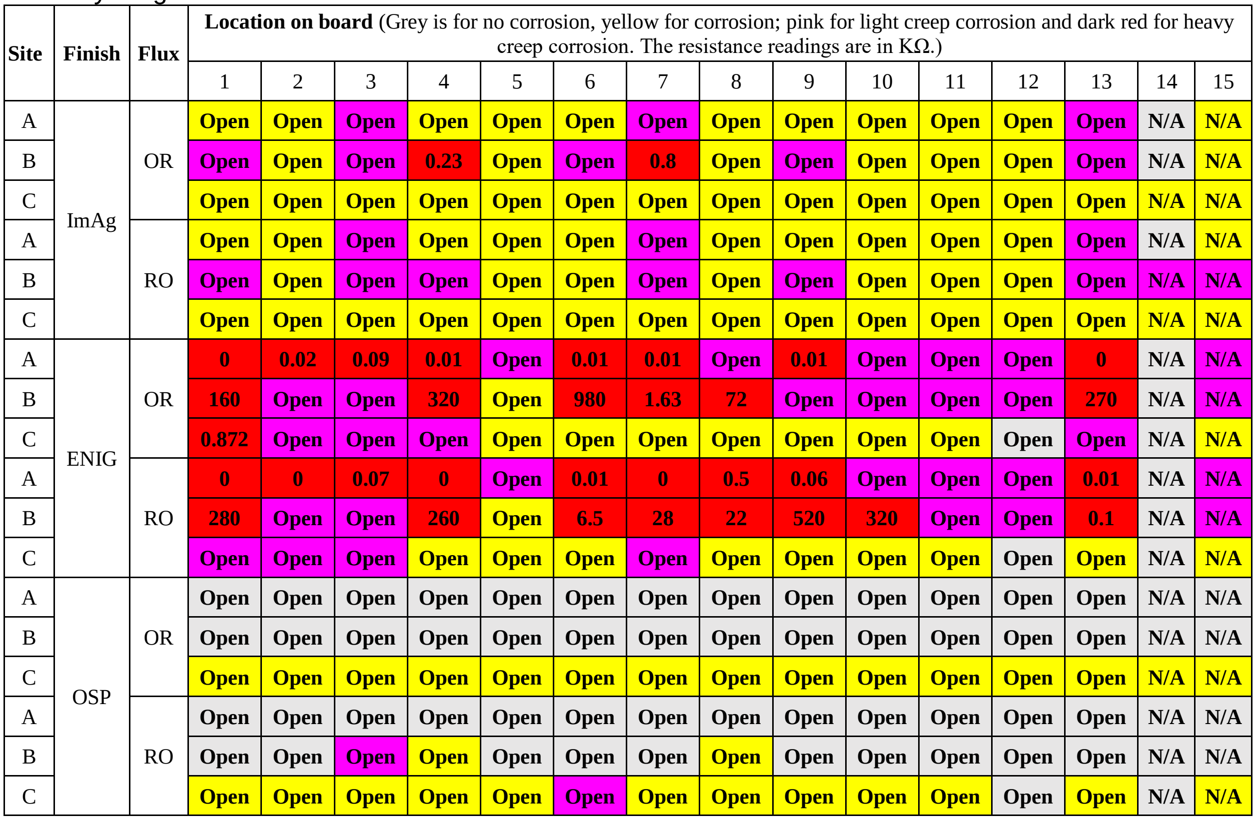
The concentrations of gases in the chamber were indirectly measured by measuring the copper and silver corrosion rates using the coulometric reduction and the mass gain methods. It was assumed that the AgCl formation rate was directly related to the chlorine concentration and that the corrosion rates of copper and silver were related to a combination of sulfur and chlorine concentrations plus the humidity and the temperature of the air. In earlier iNEMI research, it was discovered that in the relative humidity range

Table 9.2a: Corrosion map after the 1st 5 days with $MgCl_2$ saturated salt solution. The relative humidity range across three test sites was 31-45%.



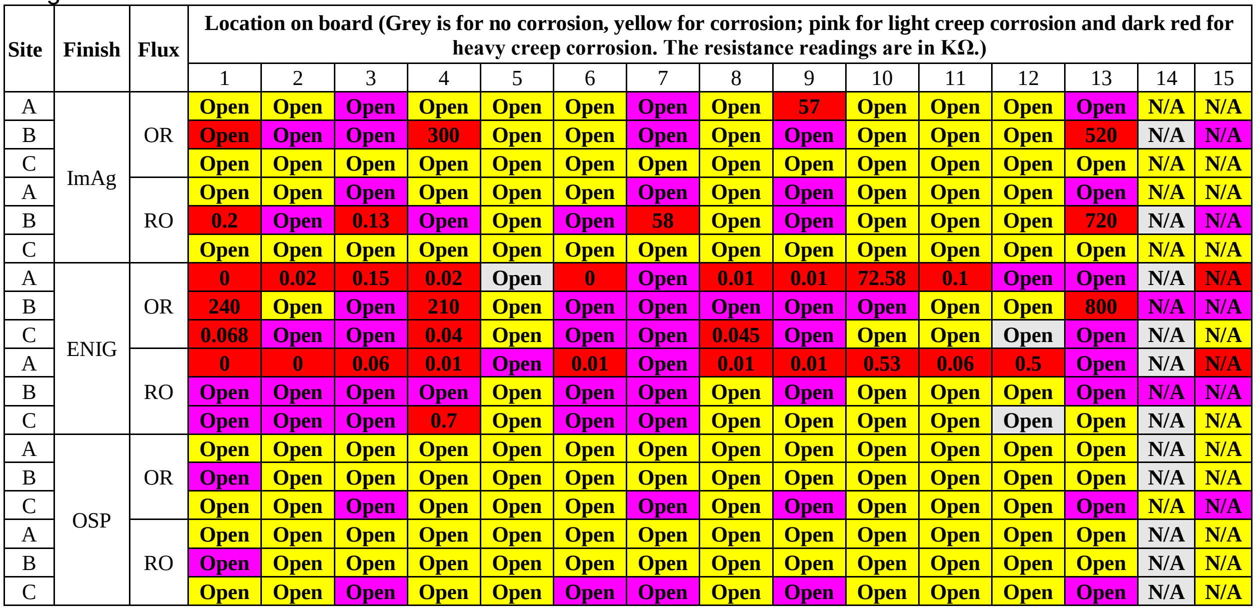
Site	**Finish**	**Flux**	**Location on board** (Grey is for no corrosion, yellow for corrosion; pink for light creep corrosion and dark red for heavy creep corrosion. The resistance readings are in KΩ.)														
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A	ImAg	OR	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
B			**0.07**	**Open**	**Open**	**0.07**	**Open**	**Open**	**53**	**384**	**25**	**Open**	**Open**	**Open**	**4.5**	**N/A**	**N/A**
C			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
A		RO	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
B			**24**	**Open**	**Open**	**Open**	**Open**	**Open**	**0.03**	**580**	**Open**	**702**	**Open**	**Open**	**0.05**	**N/A**	**N/A**
C			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
A	ENIG	OR	**0.02**	**0.23**	**21**	**0.04**	**Open**	**0.07**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**0.02**	**N/A**	**N/A**
B			**0.01**	**1**	**Open**	**0.03**	**Open**	**Open**	**0.05**	**Open**	**Open**	**Open**	**Open**	**Open**	**0.02**	**N/A**	**N/A**
C			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
A		RO	**0**	**0.44**	**Open**	**0**	**Open**	**0.07**	**0.01**	**Open**	**91**	**Open**	**Open**	**Open**	**0.01**	**N/A**	**N/A**
B			**0.05**	**0.74**	**Open**	**0.01**	**Open**	**3.7**	**0.02**	**Open**	**Open**	**Open**	**Open**	**Open**	**0.01**	**N/A**	**N/A**
C			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
A	OSP	OR	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
B			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
C			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
A		RO	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
B			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
C			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**

Table 9.2b: Corrosion map after the 2nd 5 days with NH_4NO_3 saturated salt solution. The relative humidity range across 3 test sites was 46-57%.



Site	Finish	Flux	**Location on board** (Grey is for no corrosion, yellow for corrosion; pink for light creep corrosion and dark red for heavy creep corrosion. The resistance readings are in KΩ.)														
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A	ImAg	OR	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
B			**Open**	**Open**	**Open**	**0.23**	**Open**	**Open**	**0.8**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
C			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
A		RO	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
B			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
C			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
A	ENIG	OR	**0**	**0.02**	**0.09**	**0.01**	**Open**	**0.01**	**0.01**	**Open**	**0.01**	**Open**	**Open**	**Open**	**0**	**N/A**	**N/A**
B			**160**	**Open**	**Open**	**320**	**Open**	**980**	**1.63**	**72**	**Open**	**Open**	**Open**	**Open**	**270**	**N/A**	**N/A**
C			**0.872**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
A		RO	**0**	**0**	**0.07**	**0**	**Open**	**0.01**	**0**	**0.5**	**0.06**	**Open**	**Open**	**Open**	**0.01**	**N/A**	**N/A**
B			**280**	**Open**	**Open**	**260**	**Open**	**6.5**	**28**	**22**	**520**	**320**	**Open**	**Open**	**0.1**	**N/A**	**N/A**
C			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
A	OSP	OR	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
B			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
C			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
A		RO	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
B			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
C			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**

Table 9.2c: Corrosion map after the 3rd 5 days with KCl saturated salt solution. The relative humidity range across 3 test sites was 61-78%.

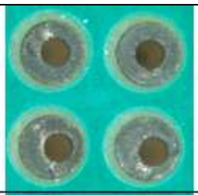
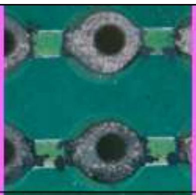
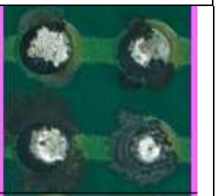
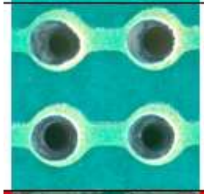
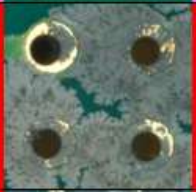
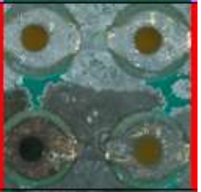
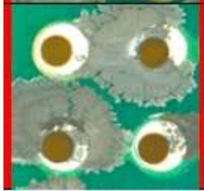
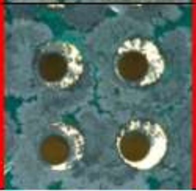
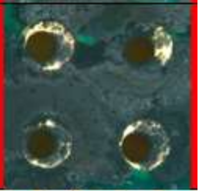
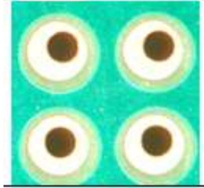
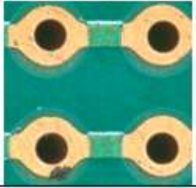
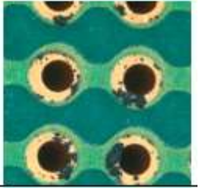
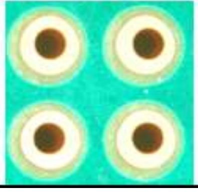
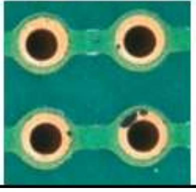
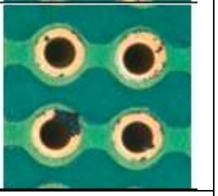


Site	Finish	Flux	**Location on board (Grey is for no corrosion, yellow for corrosion; pink for light creep corrosion and dark red for heavy creep corrosion. The resistance readings are in KΩ.)**														
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A	ImAg	OR	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**57**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
B			**Open**	**Open**	**Open**	**300**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**520**	**N/A**	**N/A**
C			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
A		RO	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
B			**0.2**	**Open**	**0.13**	**Open**	**Open**	**Open**	**58**	**Open**	**Open**	**Open**	**Open**	**Open**	**720**	**N/A**	**N/A**
C			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
A	ENIG	OR	**0**	**0.02**	**0.15**	**0.02**	**Open**	**0**	**Open**	**0.01**	**0.01**	**72.58**	**0.1**	**Open**	**Open**	**N/A**	**N/A**
B			**240**	**Open**	**Open**	**210**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**800**	**N/A**	**N/A**
C			**0.068**	**Open**	**Open**	**0.04**	**Open**	**Open**	**Open**	**0.045**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
A		RO	**0**	**0**	**0.06**	**0.01**	**Open**	**0.01**	**Open**	**0.01**	**0.01**	**0.53**	**0.06**	**0.5**	**Open**	**N/A**	**N/A**
B			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
C			**Open**	**Open**	**Open**	**0.7**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
A	OSP	OR	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
B			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
C			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
A		RO	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
B			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**
C			**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**Open**	**N/A**	**N/A**

above about 50%, corrosion rates decrease with humidity, probably because of the adsorption of chlorine gas by moisture condensed on surfaces in the chamber. This trend of decreasing corrosion rates with increasing humidity is clearly evident in **Table 9.1** especially for the AgCl growth rate. The AgCl growth rate decreases dramatically as the relative humidity is increased. The exception to this behavior is the high AgCl growth rate observed at Company B at 50-51% relative humidity. The AgCl growth rate at Company C may have been lower than that of Company A because the household bleach Company C used may have been in storage too long, well beyond its shelf life. Another Clorox bleach used by Company C contained a fragrance agent, and it also generated little AgCl. **Table 9.1** shows that, in general, there is reasonable agreement between the copper and silver corrosion rates of Companies A and C; whereas, the copper and silver corrosion rates of Company B were higher.

The creep corrosion results from the three participating companies on six different PCBs under three different humidity conditions are listed in **Tables 9.2a-9.2c**. A quick glance at the tables shows that, overall, the ENIG-finished boards suffered the most creep corrosion and the OSP-finished boards suffered the least.

Table 9.3: Worst case creep corrosion and location on test PCB.

Saturated salt		**$MgCl_2$**	**NH_4NO_3**	**KCl**
Relative humidity range		31-45	46-57	61-78
Cu corrosion rate, coul redn/mass gain, Å/day		1667/1797	604/904	687/--
Ag corrosion rate, coul redn/mass gain, Å/day		1244/1561	558/719	378/--
AgCl formation rate, Å/day		566	40	17
Finish and flux	**ImAg OR**			
	ImAg RO			
	ENIG OR			
	ENIG RO			
	OSP OR			
	OSP RO			

The red cell background indicates heavy creep corrosion and the pink cell background indicates light creep corrosion. Test results are from Company A

A major discrepancy in the results is that the ImAg-finished boards suffered heavy creep corrosion in the Company B chamber even in the low humidity range of 38-42%; while at Companies A and C, ImAg-finished boards suffered little to no creep corrosion. The explanation for the high creep corrosion on ImAg-finished boards at Company B may lie in the high levels of chlorine gas in the Company B chamber as evidenced by the high rate of AgCl formation. Overall, the creep corrosion test results from the three companies were in general agreement. **Table 9.3** shows the worst-case creep corrosion, after the three five-day tests, on the six types of PCBs tested at Company A.

The control of the FoS chamber environment is important. Instead of directly measuring the chemical composition of the gases in the chamber, it is more convenient to measure the rates of copper and silver corrosion using coulometric reduction technique. Not only does one get the formation rates of cuprous and cupric oxides, copper sulfide, silver sulfide and silver chloride, these rates are cumulative in nature, being averaged over the duration of the test. The team determined that sulfur content in the tray did not have any significant effect on copper and silver corrosion rates as discussed in an earlier section of the white paper. This result should come as no surprise because, according to thermodynamics, the equilibrium concentration of sulfur in the air in a sealed chamber is only a function of temperature. The sulfur tray can conveniently hold 200g sulfur. Therefore, the team decided to standardize the test to 200g sulfur in subsequent testing.

Chlorine concentration control is a challenge. The iNEMI test process measures chlorine concentration in the air indirectly by measuring the AgCl growth rate on silver foils. There is much variability in the rate of formation of AgCl during the five-day test runs, most probably due to variability of the chemistry of the household bleach used by the three companies. Another source of variability may be variations in the synergistic effects of chlorine, sulfur and moisture in the air on the AgCl growth rate. The study of corrosion rates as a function of Clorox dilution was discussed previously in this paper.

9.2 Second round-robin test [44]

Based on the analysis of the first round of testing, as well as the study of corrosion rates as a function of sulfur content and of Clorox dilution, the FoS test setup was finalized to include 200g sulfur and use regular concentrated Clorox with 8.25% sodium hypochlorite (see **Figure 3.2**). The same three companies participated in the second round-robin creep test.

Table 9.4: Relative humidity and corrosion rates in the three five-day test runs at the three companies (A, B and C)

Site	Saturated salt	Bleach setup gap	Relative humidity	Cu corrosion rate, Å/day, coul reduction/mass gain	Ag corrosion rate, Å/day, coul reduction/mass gain	AgCl formation rate, Å/day, coul reduction
A	$MgCl_2$	1 mm	28-30	991/1086	462/771	60
B		1 mm	42-44	940/1020	624/536	160
C		1 mm	42-43	1322/1205	1343/885	91
A	$NaNO_2$	1 mm	55-57	846/694	439/480	92
B		1 mm	55-62	470/257	895/648	48
C		1 mm	55	702/862	941/801	64
A	KCl	3 mm	81-83	1406/751	427/488	44
B		3 mm	68-75	874/557	780/968	80
C		3 mm	73-75	1118 / 960	861/1037	75

Table 9.5a: Corrosion map after the 1st 5 days with MgCl2 saturated salt solution. The relative humidity range across three test sites was 28-44%

Site	Finish	Flux	**Location on board** (Grey is for no corrosion, yellow for corrosion; pink for light creep corrosion and dark red for heavy creep corrosion. The resistance readings are in KΩ.)														
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A	ImAg	OR	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
B			250	Open	Open	730	Open	Open	Open	Open	Open	Open	Open	Open	2.16	N/A	N/A
C			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
A	ImAg	RO	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
B			20.8	Open	350	Open	Open	Open	500	300	1100	Open	Open	Open	190	N/A	N/A
C			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
A	ENIG	OR	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
B			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
C			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
A	ENIG	RO	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
B			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
C			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
A	OSP	OR	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
B			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
C			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
A	OSP	RO	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
B			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
C			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A

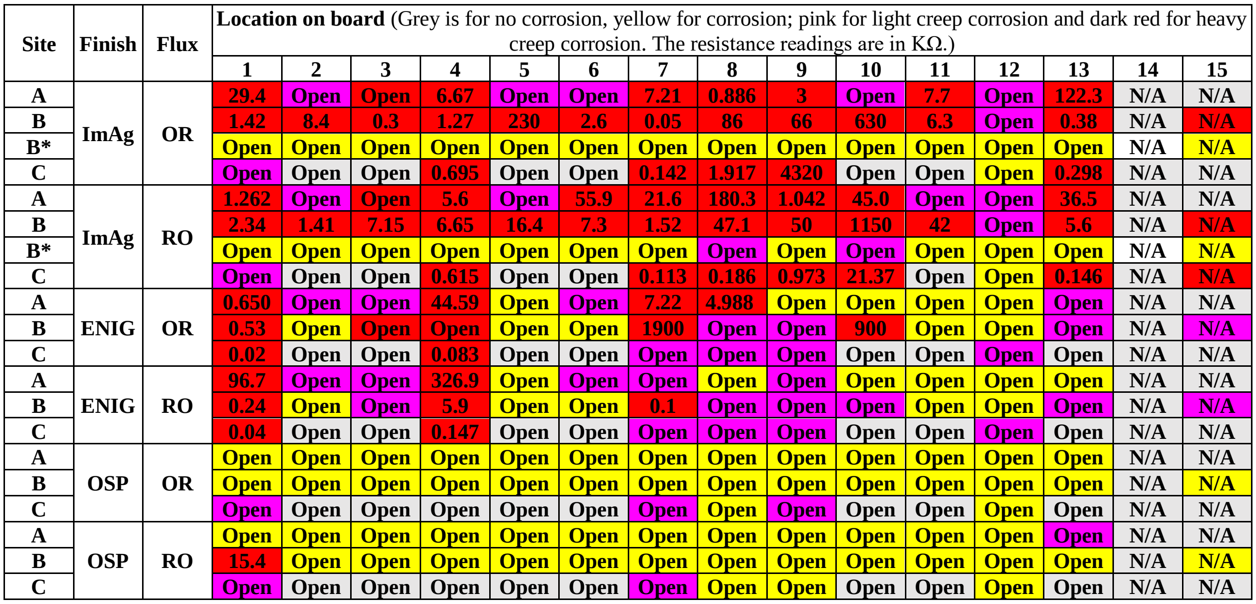
The iNEMI FOS test setup was the same as that used in round one. The only difference was that the second five-day run used a different saturated salt solution, achieving a relative humidity of 59% using $NaNO_2$ saturated salt solution.

The copper and silver corrosion rates and the rate of formation of AgCl measured during each five-day period using the coulometric reduction and the mass gain methods are listed in **Table 9.4**. The table also lists the relative humidity conditions. The extent of creep corrosion was documented after each five-day run. **Tables 9.5a-c** list the creep corrosion results for the three participating companies under the three humidity levels after each five-day test run for each of the six types of PCBs under test. At Company B, the two ImAg boards had suffered heavy creep corrosion during the first 10 days of testing. So these two boards were not subject to any further exposure in the FoS chamber Company B continued the third five-

Table 9.5b: Corrosion map after the 2nd 5 days with NaNO2 saturated salt solution. The relative humidity range across three test sites was 55-62%

Site	Finish	Flux	**Location on board** (Grey is for no corrosion, yellow for corrosion; pink for light creep corrosion and dark red for heavy creep corrosion. The resistance readings are in KΩ.)														
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A	ImAg	OR	0.70	Open	Open	71.1	Open	Open	0.725	3.8	Open	Open	2.16	Open	9.45	N/A	N/A
B			1.42	8.4	0.3	1.27	230	2.6	0.05	86	66	630	6.3	Open	0.38	N/A	N/A
C			Open	Open	Open	Open	Open	Open	0.856	285	19180	Open	Open	Open	Open	N/A	N/A
A	ImAg	RO	2.50	Open	Open	Open	Open	0.736	51.8	22	64.6	50	Open	Open	215	N/A	N/A
B			2.34	1.41	7.15	6.65	16.4	7.3	1.52	47.1	50	1150	42	Open	5.6	N/A	N/A
C			Open	Open	Open	2848	Open	Open	0.625	0.324	1.287	Open	Open	Open	0.198	N/A	N/A
A	ENIG	OR	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
B			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
C			0.633	Open	Open	0.586	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
A	ENIG	RO	Pulse	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
B			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
C			0.441	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
A	OSP	OR	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
B			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
C			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
A	OSP	RO	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
B			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
C			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A

Table 9.5c: Corrosion map after the 3rd 5 days with KCl saturated salt solution. The relative humidity range across three test sites was 68-83%



Site	Finish	Flux	**Location on board** (Grey is for no corrosion, yellow for corrosion; pink for light creep corrosion and dark red for heavy creep corrosion. The resistance readings are in KΩ.)														
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A	ImAg	OR	29.4	Open	Open	6.67	Open	Open	7.21	0.886	3	Open	7.7	Open	122.3	N/A	N/A
B			1.42	8.4	0.3	1.27	230	2.6	0.05	86	66	630	6.3	Open	0.38	N/A	N/A
B*			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
C			Open	Open	Open	0.695	Open	Open	0.142	1.917	4320	Open	Open	Open	0.298	N/A	N/A
A	ImAg	RO	1.262	Open	Open	5.6	Open	55.9	21.6	180.3	1.042	45.0	Open	Open	36.5	N/A	N/A
B			2.34	1.41	7.15	6.65	16.4	7.3	1.52	47.1	50	1150	42	Open	5.6	N/A	N/A
B*			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
C			Open	Open	Open	0.615	Open	Open	0.113	0.186	0.973	21.37	Open	Open	0.146	N/A	N/A
A	ENIG	OR	0.650	Open	Open	44.59	Open	Open	7.22	4.988	Open	Open	Open	Open	Open	N/A	N/A
B			0.53	Open	Open	Open	Open	Open	1900	Open	Open	900	Open	Open	Open	N/A	N/A
C			0.02	Open	Open	0.083	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
A	ENIG	RO	96.7	Open	Open	326.9	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
B			0.24	Open	Open	5.9	Open	Open	0.1	Open	Open	Open	Open	Open	Open	N/A	N/A
C			0.04	Open	Open	0.147	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
A	OSP	OR	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
B			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
C			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
A	OSP	RO	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
B			15.4	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A
C			Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	Open	N/A	N/A

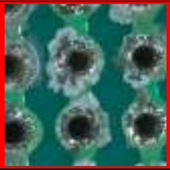
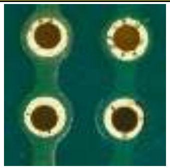
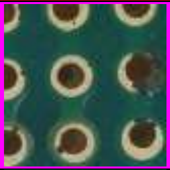
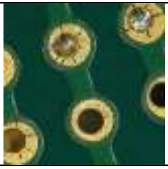
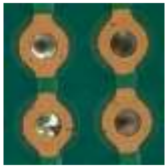
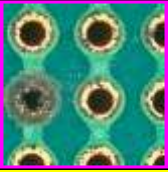
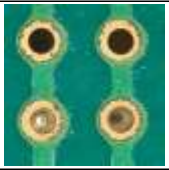
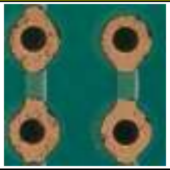
day testing p using new pre-baked ImAg boards to verify the creep corrosion sensitivity to high relative humidity. **Table 9.6a-c** shows the worst-case creep corrosion after the three five-day tests on the six types of PCBs tested at the three companies.

9.3 Summary of the two round-robin tests

The first round-robin creep corrosion tests conducted on six different test PCBs at three companies gave quite similar results with some differences, the major one being that the ImAg PCBs suffered creep corrosion at Company B while the ImAg PCBs suffered little to no creep corrosion at Companies A and C. This discrepancy may be explained by the high corrosion rates suffered by copper and silver in the Company B chamber, especially the high rate of formation of AgCl. Overall, the round-robin test results are in general agreement with the industry that among the PCB finishes tested, the OSP-finished PCBs suffered little to no creep corrosion and the ENIG-finished PCBs suffered the most creep corrosion. The second round-robin test setup and PCBs were similar for all three companies: (a) the Clorox setup gap was 1 mm for the first two five-day runs and 3mm for the third five-day run that used the KCl saturates salt solution; (b) the sulfur content was 200g; (c) the regular concentrated Clorox contained 8.25% sodium hypochlorite; and (d) the test PCBs were from the same manufacturing lot.

The second round-robin test results differed from the first in that the ImAg-finished PCBs suffered much more creep corrosion than the ENIG-finished PCBs. This difference may be a natural outcome of the aging of the PCBs as noted below where it was observed that PCBs from lots that had suffered creep corrosion in the field stopped suffering creep corrosion after two years of storage in an office environment. In other words, creep corrosion behavior changes as PCBs age. In both round-robin tests, the OSP-finished test PCBs suffered little to no creep corrosion, which is consistent with generally accepted industry wisdom.

Table 9.6a: Company A test results: worst case creep corrosion and location on test PCB

Saturated salt		**$MgCl_2$**	**$NaNO_2$**	**KCl**
pH Value (before/after)		10.8/9.47	11.0/9.47	10.99/9.17
Relative humidity (5 readings)		28-30	55-57	81-83
Cu corrosion rate, coul redn/mass gain, Å/day		991/1086	846/694	1406/751
Ag corrosion rate, coul redn/mass gain, Å/day		462/771	439/480	427/488
AgCl formation rate, Å/day		60	92	44
Finish and flux	**ImAg OR**			
	ImAg RO			
	ENIG OR			
	ENIG RO			
	OSP OR			
	OSP RO			

The red cell background indicates heavy creep corrosion and the pink cell background indicates light creep corrosion.

Table 9.6b: Company B test results: worst case creep corrosion and location on test PCB

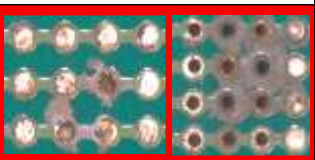
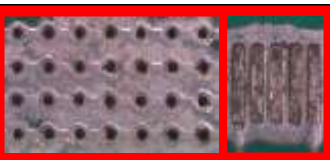
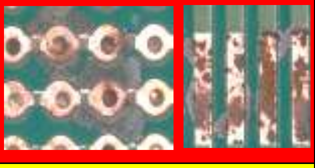
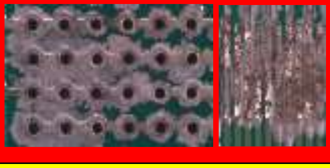
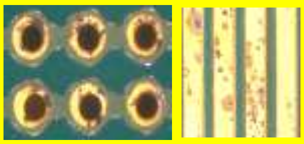
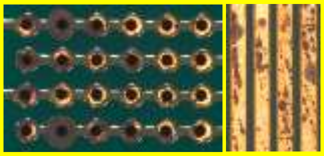
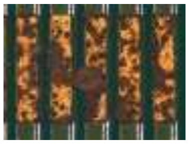
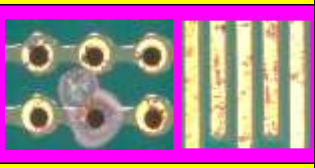
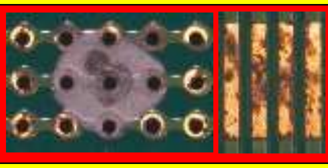
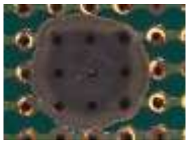
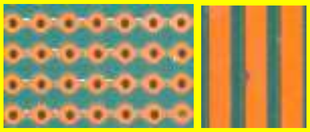
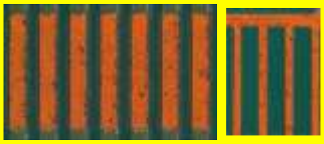
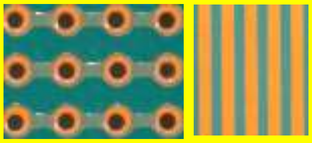
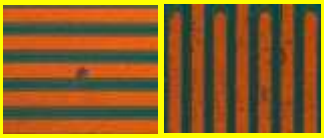
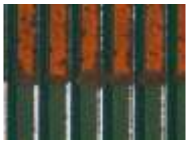
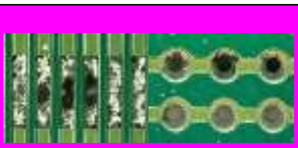
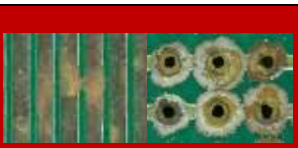
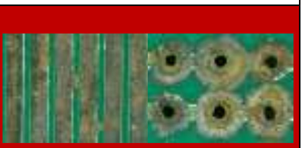
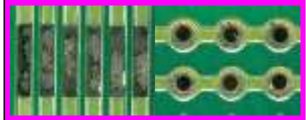
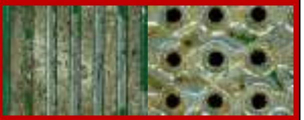
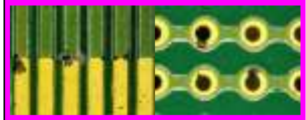
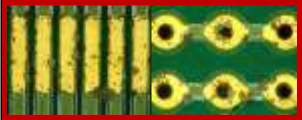
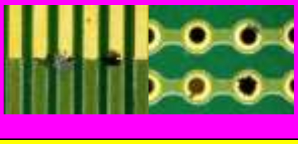
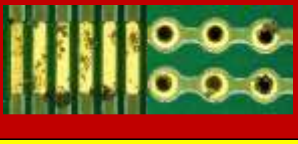
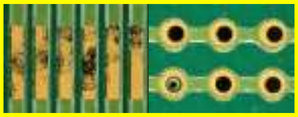
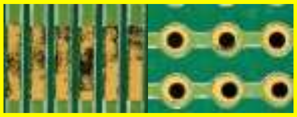
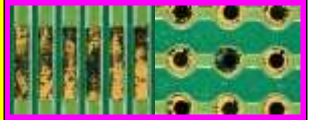
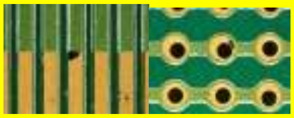
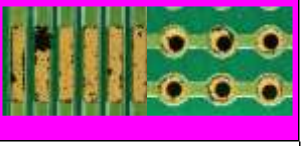
Saturated salt		**MgCl$_2$**	**NaNO$_2$**	**KCl**
pH Value (before/after)		9.61/8.68	9.2/8.9	9.4/8.9
Relative humidity (5 readings)		42%-44%	55%-62%	68-75%
Cu corrosion rate, coul redn/mass gain, Å/day		940/1020	470/257	874/557
Ag corrosion rate, coul redn/mass gain, Å/day		624/536	895/648	780/968
AgCl formation rate, Å/day		160	48	80
Finish and flux	**ImAg OR**	🟥 	🟥 	
	ImAg RO	🟥 	🟥 	
	ENIG OR	🟨 	🟨 	
	ENIG RO	🟪 	🟥 	
	OSP OR	🟨 	🟨 	
	OSP RO	🟨 	🟨 	
The red cell background indicates heavy creep corrosion and the pink cell background indicates light creep corrosion.				

Table 9.6c: Company C: worst case creep corrosion and location on test PCB.

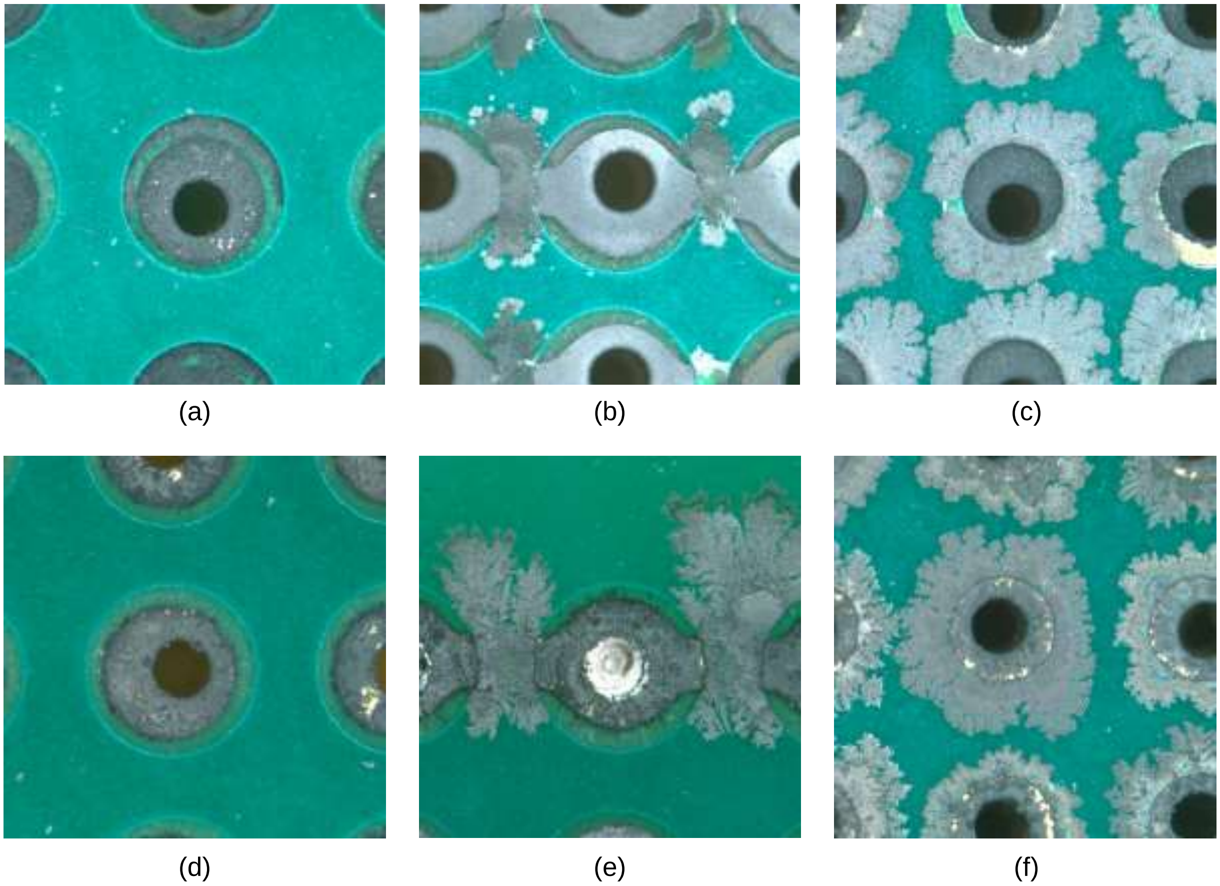
Saturated salt		$MgCl_2$	$NaNO_2$	KCl
pH Value (before/after)		9.7 / 8.7	10.2 / 9.0	9.5 / 9.3
Relative humidity (5 readings)		42-43% RH	55% RH	73-75% RH
Cu corrosion rate, coul redn/mass gain, Å/day		1,322 / 1,205	702 / 862	1118 / 960
Ag corrosion rate, coul redn/mass gain, Å/day		1,343 / 885	941 / 801	861 / 1037
AgCl formation rate, Å/day		91	64	75
Finish and flux	**ImAg OR**	🟪 	🟥 	🟥 
	ImAg RO	🟪 	🟥 	🟥 
	ENIG OR	🟪 	🟥 	🟥 
	ENIG RO	🟪 	🟥 	🟥 
	OSP OR	🟨 	🟨 	🟪 
	OSP RO	🟨 	🟨 	🟪 
The red cell background indicates heavy creep corrosion and the pink cell background indicates light creep corrosion.				

9.4 Effect of solder mask interface

Solder mask interface plays a dominant role in promoting creep corrosion as documented in **Figure 9.1**. When the copper metallization is not covered by a solder mask, as is the case in **Figures 9.1a** and **9.1d**, the tendency to creep corrosion is minimal. In cases where the copper metallization is only partially covered with a solder mask, as in **Figures 9.1b** and **9.1e**, the creep corrosion primarily emanates from the interface between the mask and the metallization. In cases where the copper metallization is completely surrounded by a solder mask, as in **Figures 9.1c** and **9.1f**, the creep corrosion radiates out from the metallization mask interface circle. The reason for the creep corrosion occurring at the metallization mask edge may be due to the solder flux or plating solution trapped at the edge. This observation is consistent with the well-known solder mask interface attack during the PCB surface finish plating, which creates a crevice at the solder mask interface. The solder mask interface crevice tends to trap electroplating chemistry and other residues, which in turn promote corrosion in the crevice. Process control for minimizing solder mask interface attack would also help to mitigate creep corrosion.

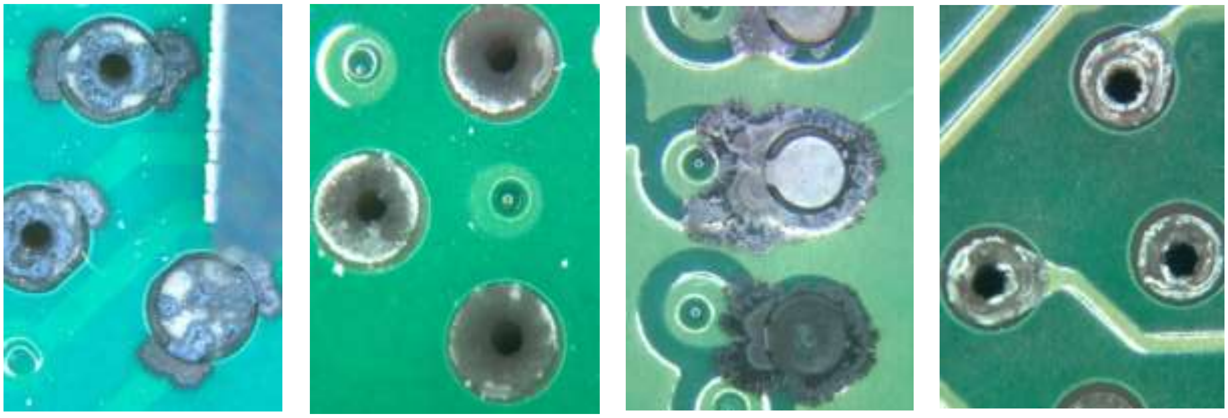
9.5 Effect of storage time

The project team found evidence that the length of time PCBAs are stored may reduce their tendency to creep corrosion. PCBAs from lots from two different companies that had suffered creep corrosion in the field were tested in the iNEMI FoS test. Fresh PCBAs, from both companies, with very short storage times, suffered creep corrosion in the iNEMI FoS test as shown in **Figure 9.2**. When stored in a normal office environment for two years and then tested, PCBAs from neither company suffered creep corrosion in the iNEMI FoS test (**Figure 9.2**). This observation of storage time reducing the tendency of creep corrosion


(a) (b) (c)

(d) (e) (f)

Figure 9.1: Role of solder mask on creep corrosion from plated-through-hole pads with exposed copper. The top three micrographs are of ImAg PCB soldered with NR330 flux from FOS run #11 with 13-19% relative humidity. The bottom three micrographs are of ENIG PCB soldered with EF8000 flux from FOS run #15 with 74-80% relative humidity. Figures **(a)** and **(d)** show no creep corrosion when the solder mask does not overlap the copper metallization. Figures **(b)** and **(e)** show creep corrosion emanating only from where the solder mask overlaps the copper metallization. Figures **(c)** and **(f)** show creep corrosion occurring all around the PTH where the solder mask overlaps the copper metallization.



fresh 2-year storage fresh 2-year storage

PCBA from one company PCBA from another company

Figure 9.2: The PCBAs from two companies suffered creep corrosion in the iNEMI FoS test when fresh. (These PCBAs were from lots that had suffered creep corrosion in the field.) After two years of storage, the sister PCBAs from these lots no longer suffered creep corrosion in the iNEMI FoS test.

may be explained if we consider that creep corrosion happens primarily at the solder mask interface. There may be processing chemicals trapped at the solder mask interface which may be the root cause of creep corrosion. Over an extended storage time, the trapped chemicals may be consumed in the reaction with the surrounding copper while at the same time forming a protective corrosion product layer. The consumption of the trapped chemicals and the passivating corrosion product layer may be the root cause hindering creep corrosion on PCBAs with extended storage time.

10. Summary

The iNEMI project on creep corrosion has developed an innovative FoS corrosion chamber that is inexpensive and easy to maintain. The temperature, relative humidity and sulfur content in the chamber air can be well controlled. The chlorine content depends on the relative humidity in the chamber and does keep rising with time. With good control of the chamber conditions, it is hoped that the chlorine concentration temporal behavior will be consistent from run to run. The importance of this corrosion chamber cannot be over emphasized considering that to remain on the Moore's law performance curve attention has shifted to packaging miniaturization through dramatic changes in packaging technologies. It behooves us to reduce the risks of these new technologies by qualify them against corrosion-related failures, especially in geographies with high pollutions levels.

In the process of developing the iNEMI corrosion chamber many discoveries and inventions were made.

- An apparatus was invented that could maintain the chamber at any humidity level in increments in the 11-90% relative humidity range, even in the presence of Clorox®, which is an aqueous solution of 8.25% sodium hypochlorite and some NaOH. The iNEMI FoS chamber currently uses Regular Concentrated Clorox to generate chlorine gas. Future work is planned to explore the possibility of using chemicals instead of Clorox.
- It was discovered that the chlorine concentration in the chamber decreases dramatically with increasing relative humidity.
- The corrosivity of the chamber air was discovered to decrease dramatically with PCB loading.

- It was discovered that prebaking the test circuit boards under flowing nitrogen gas at 100ºC for 24 hours was a necessary condition for creep corrosion occurrence in the iNEMI FoS testing. The hypothesis is that prebaking got rid of much of the VOCs.
- It was discovered that creep corrosion can occur on some PCB finishes at very low relative humidity levels and on others at high humidity levels.
- It was discovered that creep corrosion emanated mostly from where the solder mask overlapped the copper metallization.
- It was discovered that a 2-year storage period may reduce the PCB propensity to creep corrosion. This discovery was based on two production circuit boards that had suffered creep corrosion in the field and in the iNEMI FoS chamber when the PCBs were new. After 2-year storage in an office environment, the circuit boards stopped suffering creep corrosion in the iNEMI FoS chamber.

The iNEMI FoS chamber is a 300mm cube acrylic box with a paddle wheel rotating at 20 revolutions per minute (RPMs). Each paddle wheel can accommodate eight PCBs. The sulfur is contained in a 275mm square tray, 20mm deep, with a 195mm circular opening in the center. The sulfur concentration is controlled by placing the chamber in an oven maintained at a constant 50°C. Household bleach, consisting of an aqueous solution of 8.25% sodium hypochlorite with NaOH added to control the pH at about 10.8, is contained in a 145mm diameter petri dish that sits inside the sulfur tray on the same platform as the sulfur tray. The saturated salt solution is in a 190mm diameter tray with a circular opening of 65mm diameter in the center, which is covered by a circular plate with 1mm gap to allow controlled escape of the chlorine gas from the household bleach. The cover plate also throttles the escape of water vapor from the bleach such that the saturated salt solution can dominate the relative humidity in the chamber at its deliquescence relative humidity. The first step in the creep corrosion qualification test is to bake the test PCBs under flowing nitrogen gas at 100oC for 24 hours to drive off the VOCs. The test PCBs are then subject to three 5-day test runs in an iNEMI FoS chamber, inspecting the PCBs after each test run for creep corrosion: In the 1st 5-day run, the relative humidity is maintained at 31% using MgCl2 saturated salt solution; at 59% in the 2nd 5-day run using NaNO2 saturated salt solution; and at 81% in the 3rd 5-day run using KCl saturated salt solution. In each of the three 5-day test conditions, the chamber reaches steady state in a few hours. The pass-fail criterion is the occurrence of creep corrosion bridging the gap between neighboring metallization features on the test PCB.

Based on the above discoveries, inventions and development effort, a creep corrosion qualification test was developed that was successful in two round-robin testing at three companies on testing PCBs from two different lots, with three different finishes (ImAg, ENIG and OSP) soldered with two different fluxes (rosin flux and organic acid flux). In the first-round-robin, the ENIG finished boards suffered the most creep corrosion and the OSP finished boards suffered the least creep corrosion. In the second-round-robin test, the ImAg finished boards suffered more creep corrosion than the ENIG finished boards and the OSP finished boards suffered the least creep corrosion. This difference may be a natural outcome of the aging of the PCBs when it was observed that PCBs from lots that had suffered creep corrosion in the field stopped suffering creep corrosion after two years of storage in an office environment. In other words, creep corrosion behavior changes as PCBs age.

The iNEMI FoS chamber has the potential to be used as a general-purpose corrosion chamber **[43]**. It has been used to determine the corrosion rates of copper and silver as a function of temperature and humidity. This is the first through study of copper and silver corrosion rates. Conformal coatings have been characterized and ranked using the chamber by determining their resistance to sulfur gas, chlorine and moisture permeation. Another discovery was that surface-mount multi-layer ceramic capacitors with soft terminations may be very prone to corrosion-related failures in sulfur-bearing environments. Future work is considered to explore the usage of this FoS chamber for other purpose.

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APPENDIX A – iNEMI FoS Test for Creep Corrosion Procedure

First 5-day test run at 31% relative humidity using $MgCl_2$ saturated salt solution

1) Mount the test PCBs on seven of the paddle wheel slots, leaving the 8th paddle slot for a board on which Ag and Cu foils are mounted.
2) Mount cleaned and pre-weighed 25 x 50mm Ag and Cu foils on the 8th paddle to measure the Ag and Cu corrosion rates, thereby indirectly obtaining information about the sulfur and chlorine gas concentrations in the FoS chamber.
3) Add saturated $MgCl_2$ solution to the salt tray. Make sure that about one-third to one-half of the solution is undissolved salt to ensure that the solution remains saturated during the 5-day run. The depth of the solution should be no more than about 10mm as a precaution to ensure that the absorption of moisture from the air in the chamber does not cause an overflow of the solution from the salt solution tray. If the chamber is well sealed, the amount of moisture absorbed by the salt solution will be limited.
4) Add 100 ml Clorox (8.25% sodium hypochlorite) to the glass petri dish after measuring its pH, which should be about 10.8.
5) Use three 1mm thick plastic-clad spacer wires to obtain a very controlled gap between the top plate and the salt tray. This is the gap through which moisture and chlorine will escape from the Clorox petri dish.
6) Install two relative humidity (%RH) probes in the chamber.
7) Close chamber.
8) Turn on the paddle wheel to 20 rpm.
9) Turn on oven to heat to a constant 50°C.
10) Run for 5 days, measuring the %RH every day. (%RH should read close to 31%.)
11) After this first 5-day run, turn off oven, open chamber, remove the test PCBs and the copper and silver coupons. Close chamber.
12) Measure the thickness of the corrosion products on the silver and the copper foils using weight gain and coulometric reduction technique. The corrosion rate of Cu and Ag should be 500-1500 and 400-1200 Å/day, respectively. The rate of formation of AgCl should be 50-500 Å/day.
13) Scan the test PCBs and photograph and note location of the worst case creep corrosion on each PCB.

Second 5-day test run at 59% relative humidity using NaNO2 saturated salt solution

1) Mount the test PCBs on seven of the paddle wheel slots, leaving the 8th paddle for a board on which Ag and Cu foils are mounted.
2) Mount cleaned and pre-weighed 25 x 50 mm Ag and Cu foils on the 8th paddle to measure the Ag and Cu corrosion rates, thereby indirectly obtaining information about the sulfur and chlorine gas concentrations in the FoS chamber.
3) Add saturated $NaNO_2$ solution to the salt tray. Make sure that about one-third to one-half of the solution is undissolved salt to ensure that the solution remains saturated during the 5-day run. The depth of the solution should be no more than about 10mm as a precaution to ensure that the absorption of moisture from the air in the chamber does not cause an overflow of the solution from the salt solution tray. If the chamber is well sealed, the amount of moisture absorbed by the salt solution will be limited.
4) Add 100ml Clorox (8.25% sodium hypochlorite) to the glass petri dish after measuring its pH, which should be about 10.8.

5) Use three 1mm thick plastic-clad spacer wires to obtain a very controlled gap between the top plate and the salt tray. This is the gap through which moisture and chlorine will escape from the Clorox petri dish.

6) Install two %RH probes in the chamber.

7) Close chamber.

8) Turn on the paddle wheel to 20 rpm.

9) Turn on oven to heat to a constant 50°C.

10) Run for 5 days, measuring the %RH every day. (%RH should read close to 59%.)

11) After this second 5-day run, turn off oven, open chamber, remove the test PCBs and the copper and silver coupons. Close chamber.

12) Measure the thickness of the corrosion products on the silver and the copper foils using weight gain and coulometric reduction technique. The corrosion rate of Cu and Ag should be 500-1500 and 400-1200 Å/day, respectively. The rate of formation of AgCl should be 50-500 Å/day. Scan the test PCBs and photograph and note location of the worst case creep corrosion feature on each PCB.

Third 5-day test run at 81% relative humidity using KCl saturated salt solution

1) Mount the test PCBs on seven of the paddle wheel slots, leaving the 8th paddle for a board on which Ag and Cu foils are mounted.

2) Mount the cleaned and pre-weighed 25 x 50 mm Ag and Cu foils on the 8th paddle to measure the Ag and Cu corrosion rates, thereby indirectly obtaining information about the sulfur and chlorine gas concentrations in the FoS chamber.

3) Add saturated KCl solution to the salt tray. Make sure that about one-third to one-half of the solution is undissolved salt to ensure that the solution remains saturated during the 5-day run. The depth of the solution should be at least about 10mm as a precaution to ensure that the loss of moisture from the solution into the chamber does not cause the solution to become dry. If the chamber is well sealed, the amount of moisture lost by the salt solution to the chamber will be limited.

4) Add 100 ml Clorox (8.25% sodium hypochlorite) to the glass petri dish after measuring its pH, which should be about 10.8.

5) Use three 3mm thick plastic-clad wires to obtain a very controlled gap between the top plate and the salt tray. This is the gap through which moisture and chlorine will escape from the Clorox petri dish. The reason for the 3mm thick plastic-clad wire in this 3rd run is because of the much higher absorption of chlorine gas in the high humidity range.

6) Install two %RH probes in the chamber.

7) Close chamber.

8) Turn on the paddle wheel to 20 rpm.

9) Turn on oven to heat to a constant 50°C.

10) Run for 5 days, measuring the %RH every day. (%RH should read close to 81%.)

11) After this third 5-day run, turn off oven, open chamber, remove the test PCBs and the copper and silver coupons. Close chamber.

12) Measure the thickness of the corrosion products on the silver and the copper foils using weight gain and coulometric reduction technique. The corrosion rate of Cu and Ag should be 500-1500 and 400-1200 Å/day, respectively. The rate of formation of AgCl should be 50-500 Å/day. Scan the test PCBs and photograph and note location of the worst creep corrosion feature for each PCB.

Appendix B – iNEMI Position Statement on the Limits of Temperature, Humidity and Gaseous Contamination in Data Centers and Telecomm Offices to Avoid Creep Corrosion on Printed Circuit Boards (April 20, 2012)

Electronic hardware can be susceptible to creep corrosion in corrosive environments. Creep corrosion is the corrosion of metallization (generally copper and silver) and the migration of the corrosion product (typically copper and silver sulfides) across the printed circuit board (FR-4 and solder mask) surfaces. In environments high in sulfur-bearing gaseous contamination, the extent of creep corrosion may be so high as to electrically short circuit-adjacent pads and traces, causing the circuit boards to malfunction. To help eliminate creep corrosion, industry has initiated significant effort to better understand its cause and mitigation. iNEMI has had an active experimental program studying creep corrosion since October 2009.

Gaseous contamination limits for the reliable operation of electronic equipment cannot be specified in terms of the concentrations of gaseous contaminants in the air — metal corrosion is too complex a process to allow its rate to be determined from gaseous chemical composition. A more convenient and quantitative approach is the so-called “reactive monitoring” method described in ANSI/ISA-71.04-1985, *Environmental Conditions for Process Measurement and Control Systems: Airborne Contaminants* (ISA 1985). Copper and silver coupons are exposed to the environment and analyzed for corrosion product thickness. The corrosivity of the air, in terms of the rates of buildup of corrosion products on copper and silver foils, is conveniently used to indirectly define the gaseous contamination limits in data centers and telecommunication rooms.

This position statement defines the temperature, humidity and copper and silver corrosion rate limits within which PCBs will perform reliably in the field with respect to creep corrosion. These environmental guidelines are consistent with the recently published ASHRAE[1] whitepapers entitled “2011 Thermal Guidelines for Data Processing Environments” and “2011 Gaseous and Particulate Contamination Guidelines for Data Centers”.

The most effective way to protect electronic hardware from creep corrosion is to ensure that environmental conditions are within the modified severity level G1 of *ANSI/ISA-71.04-1985*:

- A copper reactivity rate of less than 30 nm /month
- A silver reactivity rate of less than 20 nm /month

The corrosion rate measurements require a minimum of one month of coupon exposure. Due to significant seasonal variations in environmental corrosivity, it is recommended that measurements be made during the season with the highest air pollution level. The most corrosive season is geography dependent but typically is in the winter months when airborne sulfur levels are the highest.

For data centers and telecommunication rooms with higher-than-acceptable copper and silver corrosion rates, corrective measures need to be taken. At a minimum, all doorways and other openings should be sealed to reduce the ingress of outdoor corrosive air. Additional measures such as gas-phase filtration of the inlet air and air in the room may be required to lower the air corrosivity to within the acceptable level. The recommended ranges for temperature and humidity are as follows:

- Temperature within 18^o to 27^oC
- Relative humidity less than 60%
- Dew point within the range of 5.5^o to 15^oC

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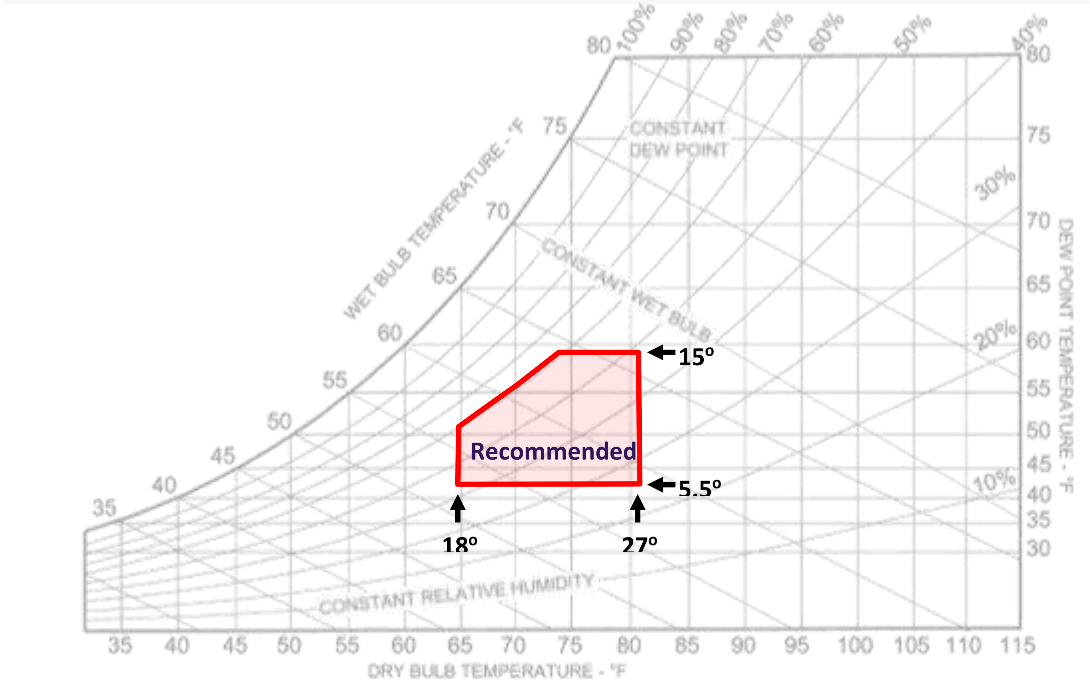
[1] American Society of Heating, Refrigerating and Air-Conditioning Engineers

The recommended range is shown in the psychrometric chart below. Adherence to these requirements is important to help maintain the high reliability of data center IT and telecommunication equipment and to minimize the cost of hardware replacement by minimizing the risk of creep corrosion. Any choice outside the recommended region will be a balance between additional energy savings of the cooling system versus the possible resulting degradation of reliability, acoustics and electrical performance. The ASHRAE 2011 Thermal Guideline whitepaper has more information on this topic.



iNEMI member companies supporting these limits:

Agilent Technologies, Alcatel-Lucent, Cisco Systems, Dell, DfR Solutions, Dow Chemical, HP, Huawei Technologies, IBM, Intel Corporation, and IST-Integrated Service Technology Inc.